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MAY, 1937

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THE MEASUREMENT OF EXTRA HARD X-RAYS AND GAMMA RAYS IN ROENTGENS¹

BY G. C. LAURENCE²

Abstract

The intensity in roentgens per second of X-rays or γ -rays harder than 0.03\AA may be measured with a small thimble chamber with homogeneous walls of elements below atomic number 13 and thick enough to be impermeable to the fastest secondary β -rays. The ionization current measured under saturation conditions at standard temperature and pressure is divided by BV , and correction is made for the apparent absorption of the X-rays in the walls. V is the volume of the chamber and B is given by

$$B = 1 + 2 \log_e (Z_w/Z_a) J/L + [2 \log_e (Z_w/Z_a)]^2 K/L + \dots$$

A table (Table IV) of the values of $2 \log_e (Z_w/Z_a)$ for different wall materials is given, and J , K , and L are plotted (Fig. 2) as functions of the quality of the radiation.

The absolute intensity of radiation in quanta per square centimetre per second may be obtained from

$$c = BL \times 2.92 \times 10^{18} \text{ e.s.u. per cc.,}$$

in which c is the ionization current per unit volume in the chamber, at standard temperature and pressure, produced by one quantum per square centimetre per second.

The intensity of the radiation from one milligram of radium in equilibrium, and covered by platinum of wall thickness t , at one centimetre distance is $(8.9_s - 1.17 \text{ mm.}^{-1} \times t)$ roentgens per hour approximately, if t is not less than 0.3 mm.

Introduction

The practical unit of X-ray quantity has been defined as follows: the roentgen shall be "the quantity of X-radiation which, when the secondary electrons are fully utilized and the wall effect of the chamber is avoided, produces in one cubic centimetre of atmospheric air at 0°C. and 76 cm. mercury pressure, such a degree of conductivity that one electrostatic unit of charge is measured at saturation current".

To avoid the wall effect of the chamber it is necessary that its dimensions exceed twice the longest range of the secondary β -rays excited by the X-rays in the air in the chamber. This is impracticable if the radiation is extra hard, for the maximum ranges increase rapidly with the potential applied to the tube from about 13 cm. at 250 kilovolts to a few metres with the highest potentials at present in use. There are a number of possible courses that might be taken to overcome this difficulty. The present unit might be abandoned and another might be chosen that is more convenient for

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very hard radiation. The unit might be changed in such a way that it is convenient for very hard radiation, but is approximately equivalent to the present unit in the measurement of soft and medium quality radiation. The unit might be retained, and practical methods of measurement might be devised that would give numerical values that differ by a negligible amount from the results that would be obtained, under certain specified conditions, by applying the present definition literally.

Many physicists who have been associated with medical radiology would regard any change in the definition at the present time as a last resort. There has been a tendency to adopt the third course of devising practical methods that are equivalent, and this has led to the use of small thimble chambers with walls that are described as air equivalent. It is supposed that the ionization per unit volume of air, enclosed by air equivalent walls, is one e.s.u. of charge per roentgen as measured at saturation current at standard temperature and pressure, after allowance has been made for the absorption of the X-rays in penetrating the walls. It is difficult to obtain this condition of air equivalence accurately in chambers constructed of ordinary convenient materials, and the ionization will differ generally by a few per cent from one e.s.u. per cc. per roentgen. However, the method is practicable if this small difference can be determined and added as a correction to the measurement. This can be done with sufficient accuracy for most purposes, by methods that will be described, if the composition of the chamber walls and the approximate quality of the radiation are known.

The density of the ionization in small chambers was first discussed by W. H. Bragg (3) in 1910, and his conclusions were reconsidered by L. H. Gray (6) in the light of the present knowledge of the properties of the rays. Gray has shown that thick walls composed of the light elements are approximately air equivalent if the radiation is sufficiently hard that there is negligible photoelectric absorption of the X-rays in the walls. The correction for the wall effect is obtained by replacing the approximations in Gray's discussion by more precise formulas.

Intensity of Ionization in Thimble Chambers

The theory and calculations in this paper are applicable when the following conditions are satisfied. The chamber is of the same material on all sides except for the insulating bushing where the collecting electrode enters. This bushing is so small that the difference in its composition from the rest of the walls can be disregarded. The collecting electrode is a fine wire, preferably aluminium, with a surface area that is negligibly small compared to the area of the walls. The radiation is so hard that the excitation of photoelectrons, by the X-rays, in the chamber and walls is negligible. The absorption and scattering of the X-rays in the walls is small, and correction can be made for the decrease in intensity due to this cause (see below). The thickness of the walls exceeds the ranges of the secondary β -rays in the wall material and, hence, excludes all secondary β -rays originating outside the chamber.

The following simplifying assumptions are made in deriving the formulas. The air space is so small that the first order excitation of β -rays in it may be neglected, and the change in velocity of β -rays in crossing the chamber can be ignored. This is justified by the experimental finding that the ionization per unit volume in small chambers is independent of the volume of the air space (5)*. The rays are uniform in intensity throughout the walls and inclosed space, and secondary X-rays arising in the walls and the air space are disregarded. Corrections for error arising from this assumption can be made in practice and are discussed later.

If the probability of converting an electron of the wall material into a β -ray of initial energy between $k_0 mc^2$ and $(k_0 + dk_0) mc^2$, and velocity in the direction given by the polar co-ordinates θ and ϕ by one quantum per square centimetre of X-rays having the direction $\theta=0$ is $f(\theta) \sin \theta d\theta d\phi dk_0$, then it follows that N , the number of β -rays produced in the material per quantum per square centimetre of X-rays, can be expressed by the relation:

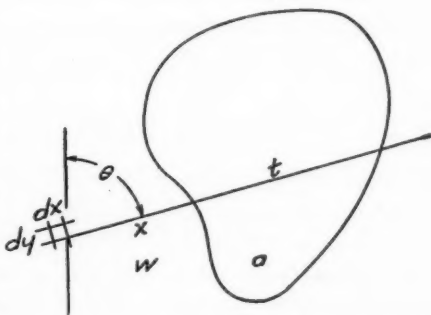
$$dN = \frac{\rho_w Z_w}{M_w} f(\theta) \sin \theta d\theta d\phi \cdot dx dy dz \cdot dk_0, \quad (1)$$

in which ρ , Z , and M are respectively density, atomic number, and mass of a single atom, and the subscript w refers to the wall material. The function $f(\theta)$ depends on θ and k_0 , but is independent of the other magnitudes.

If the dN β -particles were to continue in a straight path without deflection they would produce in the air space a number of ions, I , given by

$$dI = dN \cdot F(r_w - x) \cdot t \quad (2)$$

in which x is the distance, in the wall material, from the volume $dx dy dz$ in which the rays originate to the edge of the air space, and t is the length of the path of the particle across the air space, and r_w is the range of the β -rays of energy k_0 in the material of which the wall is constructed. The function F will be replaced later by the substitution $F=G(k)$ in which it is expressed as a function of the kinetic energy, T , ($k=T/mc^2$) of the particle as it enters the space.



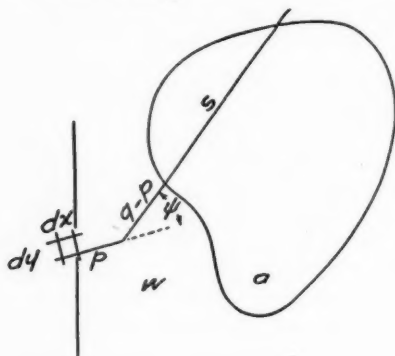
Integration of Equation (2) gives the total number of ions, I , (per quantum per square centimetre) in the air space

$$I = \frac{\rho_w Z_w}{M_w} \iiint f(\theta) \sin \theta d\theta d\phi \iiint_{r_w} F(r_w - x) t dx dy dz dk_0. \quad (3)$$

* This was also found in unpublished measurements by P. Lowe in this laboratory.

If, however, a fraction $g dp d\omega$ of the particles are deflected without appreciable loss of energy (nuclear collisions*), after traveling a distance p , in directions confined by the cone $d\omega$ making an angle ψ with the original direction, the inner triple integral of Equation (3) must be increased by the addition of the terms

$$-g dp d\omega \iiint_{r_w} F(r_w - x) t dx dy dz + g dp d\omega \iiint_r F(r_w - q) s \cos \psi dq dy dz,$$



in which q is the total distance traveled by the β -ray to the edge of the space, and s is the distance across the space in this direction. Both of these integrals are equal to

$$V \int_{r_w} F(r_w - x) dx,$$

where $\iint t dy dz = V = \iint s \cos \psi dy dz$ is the volume of the air space. Hence, the two additional terms cancel each other and the total ionization is unaffected by nuclear scattering and is expressed by Equation (3).

This is true, of course, only if all the chamber wall is of the same material throughout. Workmann (15), for example, has found a change in ionization due to reflection in chambers with ends and sides of *different* materials.

The inner triple integral of Equation (3) reduces to

$$V \int_{r_w} F(r_w - x) dx = V \int_{k_a} G(k) / \frac{dk}{dx} dk.$$

Setting $\mu_w = \iint f(\theta) \sin \theta d\theta d\phi$, and $\lambda_w = -\frac{M_w}{\rho_w Z_w} \frac{dk}{dx}$

and substituting in Equation (3) we obtain

$$I = V \int \mu_w \int_0^{k_0} G(k) / \lambda_w dk dk_0. \quad (4)$$

The intensity of the radiation in roentgens per second is equal to the rate of ionization per unit volume in the imaginary chamber, the "walls" of which are air at standard temperature and pressure. Hence the correction factor for the wall effects is

$$B = \int \mu \int \frac{G}{\lambda_w} dk dk_0 / \int \mu \int \frac{G}{\lambda_a} dk dk_0, \quad (5)$$

in which the subscript a refers to air. The subscript is dropped from μ_w and λ_a since they are equal in the absence of photoelectric excitation of β -rays. It will be more convenient to expand this equation in the rapidly converging series

* Nuclear collisions, of course, are frequently accompanied by losses of energy due to excitation or ionization that are taken into account in calculating F .

$$B = 1 + \frac{\int \mu \int \frac{G}{\lambda_a} \frac{\lambda_a - \lambda_w}{\lambda_a} dk dk_o}{\int \mu \int \frac{G}{\lambda_a} dk dk_o} + \frac{\int \mu \int \frac{G}{\lambda_a} \left(\frac{\lambda_a - \lambda_w}{\lambda_a} \right)^2 dk dk_o}{\int \mu \int \frac{G}{\lambda_a} dk dk_o} + \dots \quad (6)$$

The last term given in Equation (6) may be neglected in most cases.

The ratio G/λ_a is the reciprocal of the average loss of energy of the β -ray per ion formed, expressed in mc^2 units. It is commonly regarded as being quite accurately constant except possibly in the region below $k=0.05$, which is insignificant in the range of integration of Equation (6). This is expected on theoretical grounds (1, 14), and is supported by experiment to within the accuracy of the difficult measurement of this quantity. These measurements are discussed by Gray (6). Owing to the relative magnitudes of the terms in Equation (6) and the form of the integrands, a 1% variation in G/λ_a , over almost the entire range of integration, would produce 0.05% error in B if G/λ_a is treated as a constant. Therefore, it is justifiable to cancel it as a constant in the numerators and denominators of the second and later terms of Equation (6).

According to Bloch's (2) theory of the rate of loss of energy of the β -rays

$$\lambda = \frac{2\pi e^4 z^2}{m^2 c^4} \cdot \frac{1}{\beta^2} \left[\log_e \frac{mc^2 \beta^2 W}{1 - \beta^2} - \log P^2 Z^2 + (1 - \beta^2) + R(o) - R\left(\frac{iz}{137\beta}\right) \right]. \quad (7)$$

The symbols e , m , c , β , and z have the usual significance of electronic charge, electronic mass, velocity of light, ratio of velocities of particle and light, and the atomic number of the particle. The maximum energy that it is possible to impart to the orbital electron is represented by W , and is equal to half the kinetic energy of the β -ray. The function $R(x)$ is the real part of $\frac{d}{dx} \log_e \Gamma(x+1)$. The last two terms are negligible for β -rays when $z \ll 137\beta$.

The effective ionization potential, P , is given by $\log_e P = \frac{1}{Z} \sum a_n \log P_n$, in which P_n is the ionization potential of the n th electron shell and a_n is the corresponding oscillator strength. It is deduced, from the experimental values of λ for α -rays in penetrating gold, that $\log_e P^2 = 5.205$ (α -ray absorption is used because it is more accurate than similar β -ray data). The introduction of numerical values in Equation (7) gives

$$\lambda = \frac{2\pi e^4 z^2}{m^2 c^4} \cdot \frac{1}{\beta^2} \left[21.077 + \log \left(k^2 + \frac{k}{2} \right) - \log Z^2 + \frac{1}{(1+k)^2} \right], \quad (8)$$

in which $k = T/mc^2$, and hence,

$$\lambda_a - \lambda_w = \frac{2\pi e^4 z^2}{m^2 c^4} \cdot \frac{1}{\beta^2} \cdot 2 \log Z_w/Z_a. \quad (9)$$

The rate of loss of energy of the β -ray λmc^2 expressed in ergs per centimetre per electron per cubic centimetre of the material has been calculated by several writers. Bloch's (2) theory which is used here is in excellent agree-

ment with experimental data, as may be seen from Tables I and II, in which $s = \lambda \div 2\pi e^4 z^2 / m^2 c^4 \beta^2$ is the quantity in the brackets of Equation (8). Bethe's (1) theory, which appeared just previously, would seem to be more satisfactory in some theoretical respects, but

does not agree as well with measurement over a wide range of velocities. For example, Bethe's theory gives a value 30% too low for β -rays in mica at $\beta = 0.96$, and 100% too high for α -rays in very heavy elements. The experimental values of s are deduced from measurements by Gurney, Marsden and Richardson, and Marsden and Taylor (11, p. 140) for α -rays, and from measurements by White and Millington for β -rays (13).

Williams (14) has pointed out that White and Millington's method of determining s excludes the effects of rays that have undergone large energy losses in single collisions. He has shown that this is equivalent to setting W in Equation (7)

equal to the constant value of 1500 electron volts. (The exact value is not critical in evaluating s , since it is a factor in a large number of which the logarithm is taken.) This has been taken into account in the calculated values of s for β -rays in Table II. It was considered desirable to publish this table, because in a similar comparison of theory and experiment

TABLE I
VALUES OF s FOR α -RAYS OF VELOCITY
 1.826×10^9 CM. PER SEC. ($k = 6.6$)
IN DIFFERENT MATERIALS

Substance	s , experimental	s , calculated
H	11.5	11.69
He	9.3	10.31
(Air)	7.64	7.74
Ne	6.7	7.08
Al	6.2	6.56
A	5.9 ₅	5.91
Cu	5.0 ₃	4.96
Kr	4.5 ₈	4.52
Ag	3.7 ₆	3.99
Xe	4.02	3.71
Au	2.95	2.95

TABLE II
VALUES OF s FOR β -RAYS OF DIFFERENT VELOCITIES IN
MICA MEASURED AND CALCULATED FOR $W = 1500$ E.V.

$\beta = \frac{v}{c}$	k	s , experimental	s , calculated
0.64	3.0	10.6	10.6
0.70	4.0	10.7	11.0
0.75	5.3	11.7	11.2
0.80	6.7	12.0	11.5
0.87	10.6	13.4	11.9
0.94	19.6	12.8	12.7
0.96	25.8	13.6	13.1

that was recently published it was apparently overlooked that White and Millington's values exclude the effects of the large individual energy losses.

Substitution of Equations (8) and (9) in Equation (6) and cancellation of $\frac{G}{\lambda_a}$, as discussed previously, gives

$$B = 1 + 2 \log Z_w/Z_a \cdot \frac{J}{L} + (2 \log Z_w/Z_a)^2 \frac{K}{L} + \dots, \quad (10)$$

with

$$\left. \begin{aligned} J_s &= \int \mu \int_0^{k_0} \frac{1}{s} dk dk_0, & K_s &= \int \mu \int_0^{k_0} \frac{1}{s^2} dk dk_0, & L_s &= \int \mu k_0 dk_0 \end{aligned} \right\} \quad (11)$$

and $s = 21.077 + \log(k^2 + k/2) - 3.948 + 1/(1+k)^2$
in which the s throughout refers to air.

For monochromatic rays of energy $h\nu = \epsilon mc^2$, $K = K_*$, $L = L_*$, and $J = J_*$. For a continuous spectrum having dQ quanta in the range of quality $d\epsilon$,

$$J = \int \frac{dQ}{d\epsilon} J_* d\epsilon, \quad K = \int \frac{dQ}{d\epsilon} K_* d\epsilon, \quad \text{and} \quad L = \int \frac{dQ}{d\epsilon} L_* d\epsilon. \quad (12)$$

The integrals $\int_0^{k_0} \frac{dk}{s}$ and $\int_0^{k_0} \frac{dk}{s^2}$ are plotted as functions of $k_0 = T/mc^2$ in Fig. 1.

The values of s for very small values of k were taken directly from experimental data of electron absorption coefficients, because the theory is not valid at very low energies. The integration was performed graphically.

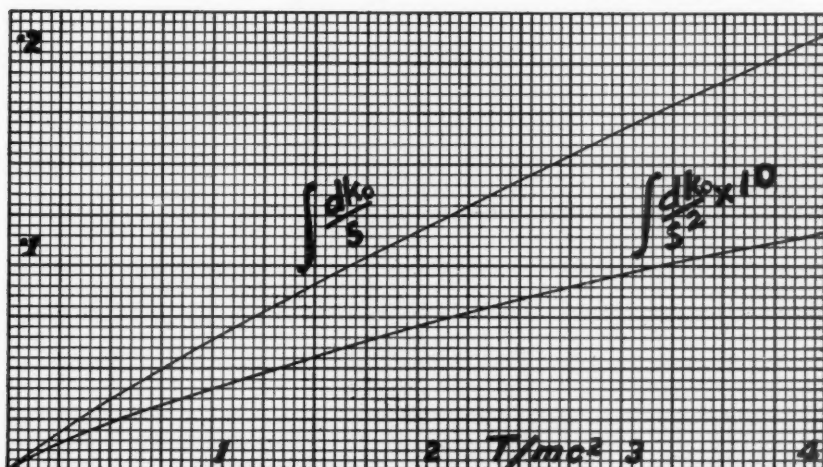


FIG. 1.

Some values of $2 \log Z_w/Z_a$ and $(2 \log Z_w/Z_a)^2$ are given in Table III. When the wall material is composed of more than one element, $2 \log Z_w/Z_a$ is replaced by $(\sum 2n_z Z \log Z/Z_a) / \sum n_z Z$, in which n_z is the relative number of atoms of the element of atomic number Z .

The number of β -rays, μdk_0 , in the energy range dk_0 , produced per electron of material by one quantum of X-rays of energy $h\nu = \epsilon mc^2$ per square centimetre is obtained by simple trigonometry from

TABLE III

Material	Z_w	$2 \log Z_w/Z_a$	$(2 \log Z_w/Z_a)^2$
H	1	-3.948	15.59
Li	3	-1.752	3.07
Be	4	-1.176	1.38
B	5	-0.730	0.53
C	6	-0.364	0.13
N	7	-0.052	0.00
O	8	0.226	0.05
F	9	0.446	0.20
Na	11	0.848	0.72
Mg	12	1.022	1.04
Al	13	1.182	1.40
S	16	2.786	7.73
Air	(7.2)	0	0
Water	(5.3)	-0.609	0.37
Bakelite	—	-0.657	0.43
Amber	—	-1.100	1.21
Cellulose	—	-0.506	0.26
Elektron	—	1.088	1.18

Klein and Nishina's (8) theory of modified scattering:

$$\mu = 4.93 \times 10^{-25} \cdot \frac{1}{\epsilon^2} \left(1 - \frac{1}{\epsilon} \frac{\xi}{\zeta} + \frac{1}{2\epsilon^2} \frac{\xi}{\zeta} + \frac{1}{2} \frac{\xi^2}{\zeta} \right), \quad (13)$$

in which $\xi = k_0/h\nu$ and $\zeta = 1 - \xi$. ($\xi h\nu$ is the energy of the scattered quantum.) The maximum value of $\xi\epsilon$ is $\frac{2\epsilon^2}{1+2\epsilon}$, and at that energy $\mu = 4.93 \times 10^{-25} \cdot \frac{1}{\epsilon} (1 + \xi\epsilon)$.

The values of J_e , K_e and L_e for one quantum of X-rays of energy $h\nu = \epsilon mc^2$ are obtained by substituting Equation (13) in Equation (11). They are plotted in Fig. 2.

Absolute Evaluation of X-ray and γ -Ray Intensities

The formulas may also be applied in the determination of intensities in quanta per square centimetre per second. The ionization current, c , per unit volume of air per second produced by one quantum of radiation of energy $mc^2\epsilon$ per square centimetre per second is, from Equation (4),

$$c = e \int \mu \int_0^{k_0} G(k) / \lambda_a dk dk_0.$$

Substitution from Equations (10) and (11) gives

$$c = e BL_e G(k) / \lambda_a.$$

The ratio $\lambda_a/G(k)$ is the loss in energy in mc^2 units per ion formed per electron in a cubic centimetre of air. Introducing numerical values, and taking the energy loss per ion as 32.5 electron volts,* we have for the current density

$$c = BL_e \times 2.92 \times 10^{15} \text{ e.s.u. per cc.}, \quad (14)$$

when the air in the chamber is at standard temperature and pressure.

Intensity of Radiation from Radium B and C

The thimble chamber method has been used in determining the intensity of the radiation, in roentgens per hour, at unit distance from 1 mg. of radium in equilibrium with its decay products, and enclosed in platinum with an effective wall thickness of 0.5 mm. Besides being an evaluation of an important constant, these measurements are a test of the reliability of thimble chamber measurements as carried out in different laboratories under different conditions. Some of the early measurements disagreed badly, but since the possible sources of error have become better understood most of the recent determinations are in good agreement when correction is made for the wall effect by the methods just described. Some very recent measurements are given in Table IV, with the experimental values reduced where necessary to 0.5 mm. platinum filtration listed in the third column, and the values fully corrected for the wall effect listed in the last column. The average of these

* See Reference (6).

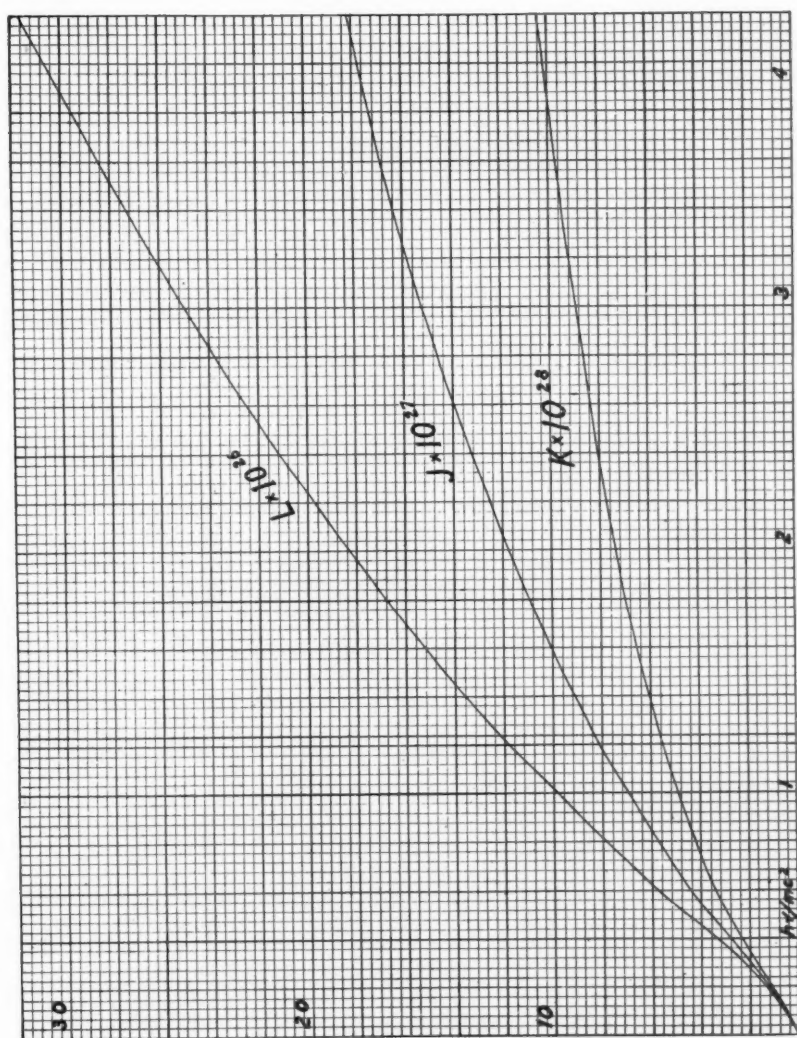


FIG. 2. Values of K , J , and L , plotted as functions of $\epsilon = \frac{h\nu}{mc^2}$.

TABLE IV
INTENSITY IN ROENTGENS PER HOUR AT 1 CM. FROM 1 MG. RADIUM IN EQUILIBRIUM
THROUGH 0.5 MM. PLATINUM

Authority	Reference	Measured intensity	Chamber wall	B	Corrected intensity
Friedrich, R. and Schulze, W.	5, p. 567	7.8	Carbon	0.977	8.0
Murdoch, J. and Stahel, E.	10	8.05	Ebonite	0.959	8.4
		8.29	Paper	0.968	8.6
Mayneord, W. V. and Roberts, J. E.	9	8.3	Carbon	0.977	8.5
Sievert, R. M.	12	7.7	Celluloid	0.968	7.9 ₅
Grimmett, L. G. and Read, J.	7	9.4	Elektron	1.074	8.6 ₅
			Mean value		8.3 ₅

is 8.3₅ roentgens per hour, and their mean deviation from the average is about 2½%. The intensity of the radiation may be expressed in more general terms, to apply to any thickness, t , of platinum wall, as

$$(8.9_8 - 1.17 \text{ mm}^{-1} \times t) \frac{\text{roentgens}}{\text{hours}} \frac{\text{mg.}}{\text{sq. cm.}},$$

with sufficient accuracy for practical purposes if t is not less than 0.3 mm.

In the calculation of J , K , and L for the γ -rays from this standard radium source, Ellis and Wooster's (4) values of the absolute intensities from radium B and C were used after correction was made for the absorption in 0.5 mm. of platinum. The amount of γ -radiation from radium and radium E and of X-radiation resulting from internal conversion and fluorescence that penetrates the platinum is negligible in these calculations. The secondary or scattered radiation arising in the platinum produces about 5% of the ionization in the chamber. Its spectral distribution was calculated approximately by the Klein and Nishina theory. It is difficult to calculate the absorption of the scattered radiation accurately because it depends on the shape of the container, but the uncertainty in J/L and K/L due to this cause is less than ¼% and has negligible significance in B .

The values obtained for the total radiation from radium in equilibrium with its decay products and enclosed in platinum with effective wall thickness of 0.5 mm. are $J/L=0.064_4$, $K/L=0.003_9$. Typical values of B with this source for different wall materials are: carbon, 0.977; elektron (90% magnesium), 1.074; aluminium, 1.081; bakelite*, 0.959; wood and cellulose products, 0.968; amber*, 0.934.

The comparison by Gray (6) of the ionization densities in chambers constructed of different materials permits a partial check of these calculated corrections. Using radium in equilibrium and filtered by 0.5 mm. of platinum and 2 cm. of lead he found, for example, that the ionization currents in aluminium and carbon chambers of the same internal dimensions were in the ratio 1.098. This agrees satisfactorily with the ratio 1.103 in the calculated values of B for these materials with the same quality of radiation.

*The following approximate compositions in relative numbers of atoms were used in calculating B : bakelite, 43 C + 38 H + 7 O; amber, 50 C + 80 H + 5 O + S.

Measurement of Extra Hard X-rays

A variety of filtrations and other conditions are used with therapeutic high voltage X-ray tubes, and B must be determined for individual cases. Approximate values that are accurate enough for many practical purposes may be estimated by inspection of Fig. 2 without carrying out the integration of Equations (12). For example, when 600 kv. is used with a filtration of 1 mm. lead and secondary filters to absorb the secondary radiation from the lead, the spectrum extends from 0.2 to 1.2 mc^2 units. At the lower limit J/L (from Fig. 2) is 0.09, and at the upper limit, 0.069. The correct value that would be obtained by Equations (12) must be between these and closer to the latter, and a good estimate is 0.07₅. If a carbon chamber is used (see Table III) $B = 1 + (-0.36 \times 0.07_5) + \dots = 0.97_3$ to within $\frac{1}{2}\%$. In more accurate calculations of B by the use of Equations (12), the spectrum must be described by $dQ/d\epsilon$ expressed as a function of $mc^2\epsilon$. In these terms, the spectrum of the radiation from the anticathode before penetrating the tube walls and filters may be represented on a graph very approximately by an oblique straight line that intercepts the $mc^2\epsilon$ axis at the point corresponding to the maximum frequency in the spectrum. If this curve is corrected for the absorption in penetrating the filters, the resulting curve will describe the spectrum transmitted with sufficient accuracy for determinations of B for ordinary purposes. (It will be seen from the discussion in the previous paragraph that B is not very sensitive to error in the shape of this curve. The difference in the spectrum from constant potential and from rectified sine wave excitation makes negligible change in its value.)

Accuracy and Absorption Corrections

The second and third terms in the expansion of B by Equation (10) are usually only a few per cent of its total value. The expressions that were used in evaluating μ and λ in these terms are probably accurate to within a few per cent, and, therefore, the uncertainty in B due to this cause is less than 0.1%. The accuracy is limited by the simplifying assumptions about absorption, scattering, and uniformity of intensity that were made in deriving Equation (10), or the accuracy with which corrections can be made for these sources of error. Absorption and scattering in the chamber wall are conveniently considered together because their combined effects can be regarded and measured as "apparent absorption". In the almost complete absence of the photoelectric effect the apparent absorption is much smaller (four times smaller in a typical case) than the true absorption, since the absorption of a quantum is accompanied by the emission of the scattered softer quantum in a direction most probably forward.

The obvious method of determining the apparent absorption is by measuring the ionization current with increasing thicknesses of chamber wall effected by adding shells of the same material on the outside of the original wall, which is of the least thickness that is impermeable to the fastest β -rays. Correction for the absorption and scattering in the walls is made then by extrapolation

to zero wall thickness. For this purpose it is very desirable that the wall and shells be of uniform thickness on all sides (and preferable that they are spherical) for the following reason. If the chamber wall is of simple shape and uniform thickness, the relative geometrical distribution of the scattered radiation is altered very little when the wall thickness is increased uniformly, and the change in the intensity of the radiation scattered from the walls is approximately proportional to the wall thickness.

The fact that the intensity of the X-rays is not quite uniform throughout the walls on account of absorption and the inverse square law, violates basic assumptions made in the derivation of the formulas, and thereby introduces a small error in the small second and third terms of B that is negligible in the total value of B for all ordinary conditions. However, the inverse square law causes a displacement of the apparent centre of the chamber towards the radiation source from the geometrical centre of the air space by a distance of the order of $\frac{1}{2}V^{\frac{1}{2}} \div R$, which is appreciable when the distance from the source is very small.

One of the most frequent measurements in radiotherapy is the determination of the skin exposure. Errors in this may be reduced by the practice of placing a slab at least 1 cm. thick of bakelite or other organic material of about the same density as flesh over the exposed skin. If this is done the skin is no longer a free surface exposed to β -rays from the filters, and the variation with depth in the tissue of the intensity of the scattered radiation is decreased. If the ionization chamber is built into this slab, the skin exposure can be obtained by correcting for absorption and inverse square law with less error than is usual in the measurement of skin dosage.

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STUDIES OF CARBON BLACK

IV. THE CHANNEL PROCESS—THE EFFECT OF DRAFT CONTROL AND CHANNEL HEIGHT ON RUBBER REINFORCEMENT, SORPTION, AND VOLATILE CONTENT¹

By L. M. PIDGEON²

Abstract

In an experimental carbon black plant of the channel type, the effect of channel height, draft control and gas composition on the properties of the carbon has been examined. The channel height was shown to be the most important variable. The rubber reinforcement and the yield of the carbon vary in a similar manner with the channel height at which the carbon was recovered. The sorption of the iodine and methylene blue increased almost logarithmically with the channel height. No direct relation between reinforcement and sorption is possible over the whole range, although the very high sorption obtained at greater channel heights was accompanied by a retarded cure. Sorption was increased by heating the blacks. The volatile content is high at low channel heights, passing through a minimum at the point of optimum yield. This test showed even poorer correlation with rubber reinforcement. Apparent density varied directly with channel height.

The effect of draft control upon reinforcement, sorption, and volatile content was indefinite. However, the volatile content seemed to vary directly with the yield. No effects characteristic of the gas composition were found.

Introduction

The properties of the carbon black from a given plant are known to be subject to daily and even hourly variations, the causes of which are either unknown or beyond the control of the operator. One of the chief reasons for the persistence of this condition is the lack of a convenient and characteristic test to evaluate and specify the properties of carbon black. The only test of quality that is satisfactory to the rubber industry consists of actually incorporating the carbon in rubber, using a test formula, followed by vulcanization and examination of the tensile properties of the resultant rubber stock. This procedure is too slow and cumbersome to be well suited to plant control.

Many attempts have been made to correlate the reinforcing action of pigments with other characteristics that are more readily measurable. Some of these tests, chiefly those concerning sorptive power and volatile content, have shown some measure of success. Where correlation has been found, however, it has been in cases where obvious differences in behavior already

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existed, such as those appearing between the broad classes of carbons. Very little information is available that correlates these tests with the rubber test and at the same time relates them to the known and controllable variables of production, such as the distance between the burner tip and depositing surface, and the restriction of draft. Until the effect of these known variables has been established, few improvements in production control can be achieved by the application of various tests to channel blacks that differ from one another for reasons unknown.

Plummer and Keller (14) examined the rubber reinforcement and iodine sorption of samples produced from propane in an experimental plant, but none of the controllable variables appeared to affect the properties of the black, unless very wide changes in operating conditions were involved. In the present work the channel height has been found to exert a very definite effect on the sorptive capacity and rubber reinforcement of the carbon.

The production of carbon black in an experimental channel apparatus was dealt with in previous papers of this series (12, 13), and the effect, on the recovery of carbon, of changes in the channel height and the draft control was examined. Both natural gas and synthetic gases containing olefines in various concentrations were employed. The production of many samples of known history presented an opportunity to examine the effect of these variables of production on the vulcanization characteristics, sorptive capacity, and volatile content of the carbons.

Reinforcement of Rubber

The carbon black samples were produced in the experimental channel apparatus that has been described previously. The effect upon yield of varying the controllable factors of production has been described in detail in previous papers of this series.

After removal from the apparatus the samples were brushed through a 100 mesh screen to break up lumps and remove any large particles. Owing to the fact that the channel used in these experiments had been ground, the scrapers were very efficient and practically no grit appeared in any of the samples.

Carbon black samples were incorporated into rubber on an open mill, using the standard diphenyl guanidine test formula described in the first paper of this series (11) (smoked sheet, 100; zinc oxide, 3; sulphur, 5; stearic acid, 2; D.P.G., 0.75; carbon, 35). The resulting compound was vulcanized in a four-cavity mold heated in a steam press to 141.5° C. for the times indicated in the tables. Tensile tests were made by two operators with dumbbell pieces in the usual manner.

Effect of Channel Height

It has been shown that the recovery of carbon from any given flame is directly dependent on the channel height, a fairly sharp maximum existing for any given flame. The tensile properties of rubber stocks containing carbon

TABLE I
EFFECT OF CHANNEL HEIGHT ON YIELD AND RUBBER REINFORCEMENT

Sample	Channel height, in.	Yield, lb. per 1000 cu ft.	Modulus at 300% elongation, kg. per sq. cm.			Modulus at 500% elongation, kg. per sq. cm.			T_B , kg. per sq. cm.			E_B , %			Hardness, (Shore)							
			85	105	125	65	85	105	125	65	85	105	125	65	85	105	125					
A. Pyrolysis waste gas. Cabot tip, 0.022 in.																						
C29	1.92	3.3	73.3	89.2	94.6	93.7	191	219	247	233	249	291	296	277	583	590	560	560	59	61	64	65
C17	2.44	4.4	91.2	104	110	107	220	243	253	243	306	302	290	262	608	570	540	518	59	61	64	65
C18	2.84	3.9	77.8	93.7	99	108	193	225	232	244	281	296	304	285	650	623	580	57	60	62	63	
C19	3.20	3.4	77.4	91	100	100	196	219	228	225	259	285	268	247	590	583	550	533	58	62	63	63
C21	3.61	2.2	61.4	72.7	80.2	85.2	154	182	194	204	191	210	228	234	567	547	548	547	56	58	60	60
B. Propane-butane (70 : 30). Cabot tip, 0.012 in.																						
C35	1.24	2.3	51.0	57.8	65.0	65.8	128	147	159	157	207	230	243	236	612	620	610	607	54	55	61	61
C36	1.64	2.8	52.0	59.0	66.0	65.0	136	152	153	159	240	243	258	251	640	630	640	607	56	57	56	61
C37	2.04	3.6	57.8	61.0	76.0	77.6	154	179	190	187	239	269	274	276	625	622	603	612	54	55	56	58
C42	2.44	4.9	93.0	100	114	125	234	253	285	292	300	312	325	305	595	552	516	59	61	62	64	
C41	2.84	3.8	71.0	80.4	93.2	102	192	213	233	247	278	300	312	308	609	607	585	587	57	57	60	63
C39	3.24	2.2	50.0	63.0	75.8	83.0	141	168	193	207	181	228	242	255	575	589	563	561	52	57	58	61
C40	3.64	1.1	40.5	47.3	56.5	66.1	117	135	162	175	167	185	205	236	578	586	566	585	51	52	55	58
C. Propane-butane (70 : 30). Cabot tip, 0.022 in.																						
C31	2.44	3.0	67.1	76.6	81.0	84.0	177	193	202	215	237	240	238	247	600	590	550	560	55	57	59	59
C32	2.84	3.9	71.6	83.0	90.0	90.0	185	206	220	220	265	277	271	265	615	600	570	565	56	58	59	59
C33	3.20	4.3	74.0	85.0	92.8	97.0	194	204	224	237	255	274	263	261	600	595	540	520	56	58	59	60
C34	3.64	3.9	66.3	77.0	87.0	89.0	177	200	219	223	252	272	290	256	590	610	595	570	54	55	57	58
C46	4.40	2.3	51.6	65.8	74.2	73.2	135	163	185	187	155	193	202	201	510	525	540	515	52	56	57	57

blacks prepared at various channel heights are shown in Table I and in Fig. 1. A very definite relation exists between stiffness and ultimate tensile strength and the channel height at which the carbon was produced. The point of maximum reinforcement corresponds approximately to the channel height at which the recovery of carbon is the greatest, so that a plot of yield against rubber reinforcement is a straight line, as can be seen in Fig. 2.

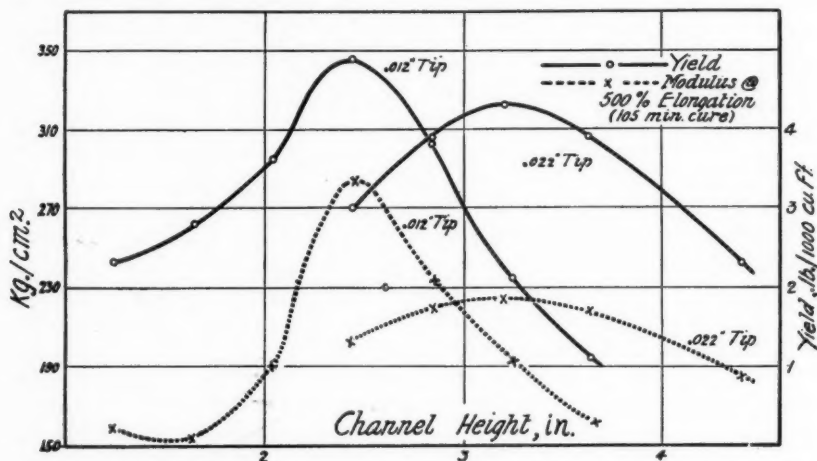


FIG. 1. Relation between rubber reinforcement, yield and channel height. Carbon black from 70:30 propane-butane.

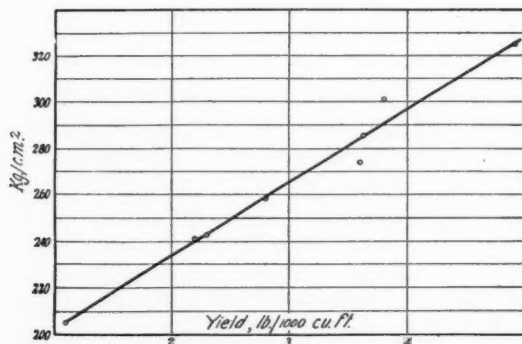


FIG. 2. Relation between yield and tensile strength (cure time, 105 min.).

Table I includes the results obtained with two gas mixtures and with two burner tips, and while the maxima appear at different positions, the relation between channel height and stiffness is similar in every case. (It should be noted that the results in Section A of Table I were obtained with a sample of raw rubber different from that used in Sections B and C.)

At great channel heights the cure was strongly retarded, so that the optimum tensile strength was not attained in the maximum cure time of 125 min. With lesser channel heights there does not seem to be much difference in the time of cure, as can be seen in Fig. 3, in which the ultimate tensile strength

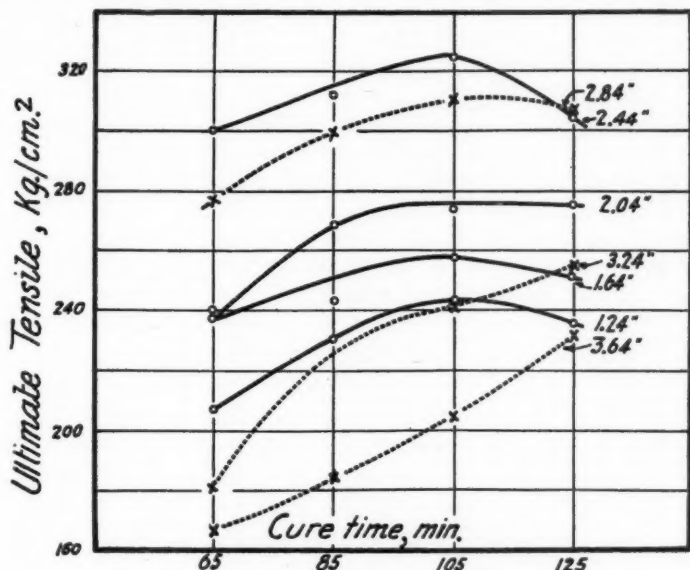


FIG. 3. Effect of channel height on rubber reinforcement.

is plotted against cure time. The curves pass through a maximum at a channel height of 2.44 in., and all except the greatest channel heights show maxima in the vicinity of 105 min. cure. The work of Plummer and Keller (14) gave no conclusive information on a relation of reinforcement to channel height, as only three channel heights were reported, but it appeared that the optimum tensile properties coincided with optimum yield.

Effect of Draft Control

It has been shown previously that the yield may be increased if restriction of the air supply in the burner chamber causes a steady burning of the flames. With unrestricted draft, convection currents cause the flames to flicker and consequently cause the yield to fall. Moderate restriction of draft improves this condition and increases the recovery of carbon. Restriction to the limit tolerated by the flame reduces the luminosity and greatly reduces the carbon recovery.

The results shown in Table II were obtained with carbon that was produced from pyrolysis waste gases. During the production of these samples the flames flickered excessively when the draft was unrestricted. The yield was increased when the drafts were closed. The reinforcing power of the carbons

TABLE II
EFFECT OF DRAFT CONTROL ON RUBBER REINFORCEMENT

Cure time, min. →		65				85				105				125				65				85				105				125			
		Yield, lb. per 1000 cu. ft.		Carbon dioxide	Oxy- gen	Modulus at 300% elongation, kg. per sq. cm.				Modulus at 500% elongation, kg. per sq. cm.				T_B , kg. per sq. cm.				E_B , %				Hardness, (Shore)											
Sample	Upper draft aper- ture																																
C22	100	3.1	1.0	19.2	74.2	89.4	98.4	101	199	218	235	235	268	279	290	278	598	568	565	537	56	63	64	62									
C23	50	3.2	1.5	17.2	72.1	85.6	94.6	97.5	183	212	222	224	245	271	291	284	600	575	590	588	57	61	60	64									
C24	38	3.5	1.8	16.3	76.2	92.0	101	102	194	224	249	242	274	300	311	290	608	598	590	558	60	61	61	64									
C18	27	3.9			77.8	93.7	98.8	108	194	225	252	244	310	319	312	328	652	625	607	597	60	61	62	64									
C25	21	3.5	3.5	14.1	83.6	98.0	102	99.5	210	242	249	238	258	321	313	306	563	598	583	578	60	64	61	57									

Pyrolysis off-gas. Channel height, 2.84 in.

TABLE III
RUBBER REINFORCEMENT BY COMMERCIAL SAMPLES

Cure time, min. —→		65	85	105	125	65	85	105	125	65	85	105	125	65	85	105	125				
Commercial sample		Modulus at 300% elongation, kg. per sq. cm.				Modulus at 500% elongation, kg. per sq. cm.				T_B , kg. per sq. cm.				E_B , %				Hardness, (Shore)			
A	62.2	78.3	85.6	96.4	161	195	210	222	228	271	285	280	608	609	605	580	56	58	61	61	
B	56.5	75.0	79.8	88.5	153	185	199	215	235	272	276	280	625	620	605	585	55	56	61	61	
C	58.2	73.7	79.1	87.3	153	188	196	211	234	270	279	278	630	610	618	590	56	59	61	63	

again follows the yield, passing through a maximum at approximately the same draft setting. The differences are rather small, however, and suggest that, as in the case of the yield, the draft control is a secondary factor.

Speed of Channel Motion

Drogin (5) has mentioned that the amount of heating to which the carbon is subjected will affect its color and even the rate of cure in a rubber mix. In the channel process the carbon is deposited in successive layers which continue to be built up until removal by the scraper. In large-scale practice, any given section of the channel moves across a number (10 to 20) of burners before passing over a scraper. It might be expected that the thickness of this layer would play an important part in the recovery and quality of the carbon, since, owing to the excellent insulating properties of carbon black, it will affect the temperature of deposition and the temperature of the channel in any given apparatus. In the experimental plant the number of flames playing on any given section of the channel is much smaller than in full-scale practice, but by reducing the speed of channel motion it is possible to produce a relatively thick layer of carbon before it is removed by the scraper.

The effect of channel speed on the properties of the carbon is shown in Table IV. In spite of the different conditions under which these samples were obtained, very little difference in their rubber reinforcement is observed.

TABLE IV
EFFECT OF CHANNEL SPEED

Sample	Channel speed, in. per min.	Modulus at 500% elongation, kg. per sq. cm.				T_B , kg. per sq. cm.				E_B , %			
		65	85	105	125	65	85	105	125	65	85	105	125
Cure time, min.→													
C 26	2.9	204	229	241	243	302	303	302	296	633	605	578	567
C 18	1.8	194	225	232	244	310	319	312	328	652	625	607	597
C 27	0.9	215	245	242	237	295	316	302	287	618	598	573	560

Pyrolysis waste gas. Channel height, 2.84 in. Draft, 27%.

Effect of Gas Composition

It will be observed that rubber tests have been carried out with carbon blacks produced by the partial combustion of paraffin gases and gases containing fairly large proportions of olefines and hydrogen. No important difference between either the magnitude of the results or their general trend has been observed.

In Table III the results of rubber tests of certain standard commercial rubber blacks are shown. The reinforcement is in all cases similar to that produced by the average sample of experimental black, and somewhat inferior to the best.

Sorption

The sorptive power of a finely divided solid affords one of the most useful tests with which to describe and specify the properties of the substance. The amount of any sorbate which will be taken up depends obviously on (i) an intensity factor, which represents the actual affinity between a given surface and the sorbate; and (ii) a capacity factor, which indicates the amount of surface available or, in other words, the shape and size of particle. Both of these factors are concerned in the reinforcing power of carbon black, and the dominant position that this filler has rapidly assumed in the rubber industry is due to both (i) and (ii). The particle size is smaller than that of any other known filler, while the "affinity" or "bond" between carbon black and rubber must be such as almost to suggest the formation of a carbon-carbon bond with rubber. (Lithopone, for example, of reasonably small particle size, exerts little reinforcing action, owing presumably to poor "affinity".) These factors are measured simultaneously when the sorptive power of a carbon black is determined, and, in fact, it is almost impossible to separate them by this test alone.

Other ingredients of a rubber compound may be adsorbed by carbon black because the carbon black presents a large surface for sorption. When ingredients thus adsorbed include the accelerator, or other agents essential to the vulcanization reaction, a retardation of cure results.

Many attempts have been made to relate the cure time with the sorptive power of the carbon, because a direct correlation would be of inestimable value to the rubber chemist. A survey of the literature soon shows that the results have not been promising. Fromandi (6) examined the sorption of acetic acid and could find no correlation with vulcanization characteristics. Spear and Moore (16) found no basic relations between the stiffness of a rubber stock and the sorption of acid or basic dyes. Ditmar and Preusse (3) and Goodwin and Park (7) found a retarding effect when sorption was high, and suggested removal of sulphur or some other essential constituent of the vulcanization reaction as the cause.

Wiegand and Snyder (20), Drogin (4), and Amon and Estelow (1) assumed that the retardation is due to accelerator sorption; they used the sorption of diphenyl guanidine as the basis of a test. In most cases it was found that a sorption test readily separated and distinguished the broad classes of carbon black, but was barely able to distinguish between individual members of a group.

A puzzling phenomenon was observed by Carson and Sebrell (2) who found that blacks that had been heated to 900° C. exhibited increased sorption accompanied by a more rapid curing rate. (Wiegand (17) has obtained a patent covering the heating of black to accelerate the cure, but his specification also states that the sorptive power is reduced.) More recently Schoenfeld (15) has suggested that the sorption by carbon black may be of the activated type. His results indicate that certain acidic impurities present ordinarily in carbon black inhibit the cure, and their removal at high temperatures results in more rapid cure, even though the sorptive power is enhanced.

In most of the work that has been carried out on this subject, it has been customary to select a certain number of samples known to differ in vulcanization characteristics, and to attempt to find similar differences in the sorptive power. The actual samples were unrelated and frequently obtained from various sources, while the differences in details of production responsible for the measured differences in vulcanization characteristics were generally unknown. The author has been able to produce a series of samples, the rubber reinforcement of which varies in a regular manner and is related to the conditions under which the samples were produced. An opportunity was therefore offered to examine the relation between reinforcement and sorption under such circumstances that the existence of any correlation could be readily detected.

Previous workers have employed organic accelerators, dyes, acids, alkalis, and even water itself to determine the sorptive power of carbon black. Iodine and methylene blue have been chosen in this research since they may be readily estimated in solution, and represent such widely different types of molecule that any relation appearing in both cases may be considered to be a general sorption phenomenon and not a reaction peculiar to any given sorbent and sorbate.

Methylene Blue

The sample of carbon black was shaken for one hour with 0.025% aqueous solution of methylene blue. (Times up to three hours gave similar results.) In the standard test 0.25 gm. of sample in 50 cc. of solution was used, but other concentrations were also employed to determine the sorption isotherm. The concentration of the subsequent solution was measured colorimetrically after separation of the carbon black. Centrifuging and filtration were both employed; similar results are obtainable with both methods if precautions are taken to ensure that the filter paper is saturated with dye at a concentration that is in equilibrium with that of the filtrate. In practice the colorimetric determination was carried out on successive fractions until constant readings were obtained.

Iodine

Carbon (0.25 gm.) was shaken for 30 min. with 50 cc. of 0.01 *N* iodine-potassium iodide solution in a glass-stoppered bottle. The mixture was then centrifuged and 10 cc. of the clear supernatant liquid titrated with 0.01 *N* thiosulphate. The amount of sorption was calculated from the concentration of the final solution.

Sorption Index

In most of the work done on sorption by carbon black it has been customary to submit the samples to some standard test similar to those described. That is, the sorption isotherm showing the amount sorbed when the carbon is in equilibrium with solutions of various concentrations was not fully determined.

Since the isotherms for a number of closely related samples are likely to be affine, this procedure is justifiable, but a serious error is frequently introduced by neglecting to compare the amounts of sorption at the same final concentration. Samples of higher sorptive power will produce more dilute solutions which in turn prevents them from showing the full extent of their sorptive capacity. Goodwin and Park (7) overcame this difficulty by adjusting the volume of the solution to compensate for the differences in sorptive power of the samples, so that a standard end point was produced in every case. This method, while capable of considerable accuracy, is cumbersome, owing to the time required to attain equilibrium after alteration of the concentration of the solution.

A basis for comparison has been obtained by dividing the amount of sorption in milligrams per gram of black by the concentration of the final solution. Thus a sample of high sorption will have its $\frac{x}{m}$ divided by a number corresponding to a low concentration. The result is termed the "sorption index" and offers a convenient means of compensating for the discrepancies in final concentration when the sorption characteristics of the carbon are measured by means of a single determination at one concentration.

Effect of Channel Height on Sorption

The sorption of methylene blue by samples produced from methane and various other hydrocarbon gases is shown in Tables V and VI. In every case the amount of sorption increased with increase in channel height. The relation is approximately logarithmic, and at the greatest channel heights very high values of sorption are attained. (At this point the sorptive power is still very much inferior to that of a good decolorizing carbon, which gives

TABLE V
EFFECT OF CHANNEL HEIGHT ON SORPTION OF METHYLENE BLUE

Sample	Channel height, in.	Yield, lb. per 1000 cu. ft.	x/m , mg. dye per gm. of carbon	Sorption index
<i>A. Carbon black from Turner Valley gas. (For details see Reference (12))</i> <i>Cabot, 0.10 in. slot: rate, 2.46 cu ft. per hr.</i>				
20	1.25	0.7	26.2	2.3
21	1.50	1.2	31.9	3.3
15	1.75	1.3	37.5	5.9
19	2.00	0.7	44.8	17.2
23	2.25	0.3	46.2	24.6
<i>B. CH₄, 85; C₂H₆, 13.5; N₂, 1.5%. Cabot, 0.022 in. slot: rate, 4.6 cu ft. per hr.</i>				
1	1.50	0.4	32.4	3.7
2	1.75	0.6	35.6	5.0
3	2.00	1.0	41.2	9.3
4	2.25	1.1	42.0	10.5
5	2.50	0.9	47.5	39.5
6	2.75	0.7	48.8	81.3

TABLE VI
RELATION BETWEEN SORPTION AND RUBBER REINFORCEMENT

A. Carbon black from propane-butane (70 : 30) (for production details see Reference (13))

Sample	Channel height, in.	Yield, lb. per 1000 cu. ft.	x/m , mg. methylene blue per gm. of carbon	Sorption index	Modulus at 500% elongation	T_B , kg. per sq. cm.
C36	1.64	2.8	16.8	1.0	258	153
C37	2.04	3.6	20.8	1.4	274	190
C38	2.44	4.9	25.2	2.0	325	285
C41	2.84	3.8	37.6	5.9	312	233
C39	3.20	2.2	40.0	8.0	242	193
C40	3.64	1.1	47.6	39.6	205	162

B. Carbon from pyrolysis off-gas: C_2H_2 , 1.2; C_2H_4 , 23.0; C_3H_6 , 11.0; H_2 , 14.8; C_nH_{2n+2} , 50.0% ($n = 1.1$)

Sample	Channel height, in.	Yield, lb. per 1000 cu. ft.	Modulus at 500% elongation	T_B , kg. per sq. cm.	x/m , mg. methylene blue per gm. of carbon	Sorption index	x/m , mg. iodine per gm. of carbon	Sorption index
C29	1.92	3.3	247	296	30.8	3.2	90.8	1.2
C17	2.44	4.4	253	290	36.8	5.6	104.0	1.5
C18	2.84	3.9	232	304	37.6	6.1	116.4	1.8
C19	3.20	3.4	228	268	41.6	9.7	128.8	2.3
C21	3.61	2.2	194	228	46.6	21.2	142.4	2.9

Cure time, 105 min.

an index of infinity by the standard test.) While the magnitude of the values are different, the relation between channel height and sorption is similar in all cases, as shown also in Fig. 4. (Carbon produced from methane appears to be a more active sorbent than that from "richer gases".) The same order is obtained when iodine is used, so that the relation between channel height and sorption may be regarded as a general one.

While the author is unaware of any other published work in which a similar relation has been described, it is of interest to note that Wiegand (18) states that the black deposited on the centre of the channel shows lower sorption than that deposited near the edges. This centre position, which is, of course, nearer to the burner tip, corresponds to a lower channel height than does the edge.

It has been pointed out previously in this series that particles of smallest size are likely to be produced when the temperature of the "cracking" zone is very high and the time of contact correspondingly short. Casual inspection of the flame will indicate that this condition is achieved at relatively high channel settings when the flame is less cooled by the channel. Quantitative measurements of this effect are being made and will be reported subsequently.

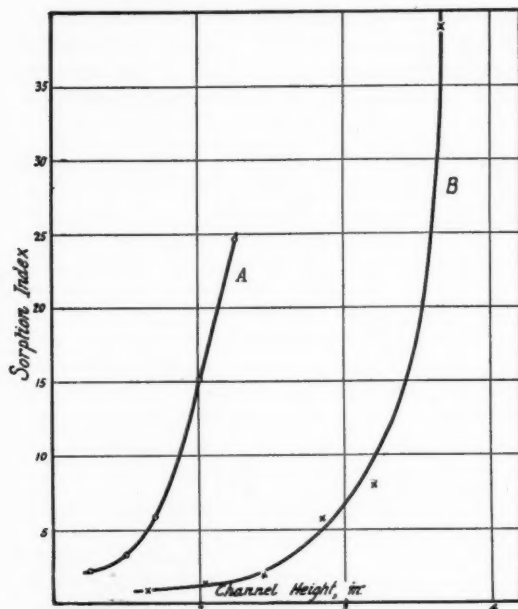


FIG. 4. Relation between channel height and sorption. A, carbon black from Turner Valley gas (15). B, carbon black from 70:30 propane-butane.

Relation Between Sorption and Rubber Reinforcement

It has been shown that the reinforcement by a series of carbon blacks passes through a maximum as the channel height at which they are produced passes from a minimum to a maximum, being relatively poor at the lowest and highest channel heights employed. Comparison of this behavior with sorption (Table VI) indicates that, considering the whole range of channel heights, no correlation exists between the tests. For example, the carbon obtained with a channel height of 2.84 in. produced an ultimate tensile strength of 312 kg. per sq. cm., and showed a corresponding sorption index of 5.9. The sample obtained at 2.04 in. broke at 274 kg. per sq. cm. and had a lower sorption index, 1.4.

The test is not completely useless, however, since the sorption at very great channel heights was very much greater and the corresponding rubber test showed strongly retarded cures. A direct relation existed between sorption and stiffness for any given cure time, in the case of blacks produced from pyrolysis off-gas, between the channel setting productive of maximum yield and the greatest setting employed.

These results show clearly why the sorption test is of limited use when applied to ordinary channel blacks. Commercial rubber blacks are likely to be made at channel settings that produce the optimum yield, and the variations that take place are probably due to changes in the effective channel

height brought about by atmospheric disturbances or fluctuations in gas pressure, both of which affect flame size, and, therefore, alter the relative position of the depositing surface. Rubber reinforcement falls off on either side of the optimum channel height, while sorption increases continuously in intensity as the channel height is increased. It is possible, therefore, to find two samples showing identical reinforcement yet varying widely in sorptive capacity. On the other hand, while a sample showing low sorption may not necessarily exhibit good rubber properties, very high sorption is almost certainly an indication of cure retardation.

Effect of Draft Control

It has been shown that the differences in draft control that may be brought about in the experimental apparatus have very little effect on the rubber properties of the carbon. A small regular difference in sorption is noticed, the direction being such that sorption increases slightly with draft restriction, and falls off again at the highest restriction possible. This effect is clearly shown in Tables VII and VIII.

In view of the large differences in sorptive power which may exist without corresponding differences in rubber reinforcement, it may be said that draft control has no significant effect on sorption.

TABLE VII
EFFECT OF DRAFT CONTROL ON SORPTION

Sample	Draft aperture	x/m , mg. methylene blue per gm. of carbon	Sorption index
<i>0.010 in. slot</i>			
52	100	42.0	10.5
53	50	44.9	17.9
56	38	46.4	25.8
60	21	40.0	8.0
<i>0.012 in. slot</i>			
15	100	37.5	5.9
24	79	41.2	9.4
25	50	41.2	9.4
26	30	41.2	9.4
16	21	33.6	4.5

Carbon from Turner Valley gas; channel height, 1.75 in.

TABLE VIII
EFFECT OF DRAFT CONTROL ON SORPTION

Sample	Draft aperture	Flue gas		x/m , mg. methylene blue per gm. of carbon	Sorption index	x/m , mg. iodine per gm. of carbon	Sorption index	T_B , kg. per sq. cm.	Modulus at 500% elongation
		Carbon dioxide	Oxygen						
C22	100	1.0	19.2	38.8	6.9	105.6	1.6	290	235
C23	50	1.5	17.2	39.4	7.4	121.6	2.0	291	222
C24	38	1.8	16.3	39.6	7.6	116.4	1.9	311	249
Bulk	27	—	—	37.4	5.9	116.4	1.9	312	232
C25	21	3.5	14.1	37.4	5.9	100.0	1.4	313	249

Carbon from pyrolysis off-gas (composition as in Table VI, B). Cabot tip, 0.022 in. slot; rate, 6.0 cu ft. per hr.; channel height, 2.84 in.; cure time, 105 min.

Effect of Channel Speed

Rubber reinforcement is little affected by the speed at which the channel moves in the experimental plant, while sorption is slightly increased by the continued heating which results from a slow moving channel, as shown in Table XI. In view of what has gone before, these differences may be regarded as negligible.

TABLE IX
EFFECT OF CHANNEL SPEED ON SORPTION

Sample	Channel speed, in. per min.	Modulus at 500% elongation, kg. per sq. cm.	T_B , kg. per sq. cm.	x/m , mg. iodine per gm. of carbon	Sorption index
C26	2.9	241	302	116.4	1.9
C18	1.8	232	312	116.4	1.9
C27	0.9	242	302	124.4	2.2

Pyrolysis waste gas; channel height, 2.84 in.; cure time, 105 min.

Miscellaneous Blacks

For purposes of comparison a number of standard commercial carbon blacks have been examined. The results are shown in Table X. The sorption test gives no useful information, since the differences between the blacks are too small to be of significance. The thermax carbon, "Thermax", shows very little sorption, a fact already well known (7). The commercial

TABLE X
SORPTION BY VARIOUS CARBON BLACKS

Sample	x/m , mg. methylene blue per gm. of carbon	Sorption index	x/m , mg. iodine per gm. of carbon	Sorption index	T_B , kg. per sq. cm.	Modulus at 500% elongation, kg. per sq. cm.
Commercial B	33.6	4.7	100.8	1.4	285	210
Commercial A	32.0	3.6	97.2	1.3	279	196
Thermax	9.2	0.5	21.2	0.2	215	159

Cure time, 105 min.

blacks show sorption values that are very similar to those of the best experimental blacks obtained in this research, but as is shown in Table II, their rubber reinforcement is somewhat inferior.

Effect of Gas Composition on Sorption

Carbon black has been produced from a number of hydrocarbon gases and from mixtures of gases, as described previously, and the sorptive properties of a number of these carbons have been examined. The results, shown in Table XI, fail to indicate a relation between sorption and the composition of the gas supplied to the flame. Any differences that appear are probably

TABLE XI
EFFECT OF GAS COMPOSITION

Ethylene	Methane	Hydrogen	Yield, lb. per 1000 cu. ft.	x/m , mg. methy- lene blue per gm. of carbon	Sorption index
100	—	—	4.3	35.6	4.9
90	—	10	4.2	37.6	6.0
85	—	15	3.4	35.6	4.9
10	90	—	1.7	34.4	4.4
25	75	—	2.0	30.0	3.0
—	90	10	0.8	36.0	6.0
—	100	—	1.3	37.5	5.9

Cabot, 0.012 in. slot; gas rate, 2.7 cu. ft. per hr.; channel height, 1.75 in.; upper draft, 21.0% open.

due to changes in the height of the flame which, owing to greater spreading over the channel, has the effect of altering the effective distance of the depositing surface. The similarity in sorption index is rather striking in view of the large differences in yield, which means that the amount of carbon deposited per unit of time was different in each case.

Effect of Heating on Sorption

A number of samples were heated to 950° C. *in vacuo* for seven minutes and then their sorptive power was measured. The results are shown in Table XII, where it will be seen that in almost every case the sorptive power

TABLE XII
EFFECT OF HEATING ON SORPTION AT 950° C. *in vacuo*

Sample	Methylene blue			Iodine		
	x/m , mg. per gm. of carbon	Sorption index	Sorption index (unheated)	x/m , mg. per gm. of carbon	Sorption index	Sorption index (unheated)
C29	38.0	6.3	3.1	175.2	5.3	1.2
C17	39.6	7.6	5.6	145.2	2.5	1.5
C18	40.8	8.9	6.0	195.2	8.6	1.8
C20	44.8	17.2	11.2	180.4	6.0	2.4
C21	45.6	21.0	21.2			
C23	39.6	7.6	7.4			
C24	38.0	6.3	7.6			
C25	34.0	4.2	5.9			

of the sample has been increased by heating. This supports the findings of Carson and Sebrell (2). The increase in sorption was much more marked with iodine than with methylene blue, a fact that may be connected with the difference in size of these molecules. Methylene blue, owing to larger molecular dimensions, may be less able than iodine to avail itself of the increased surface formed by removal of volatile matter.

The increase of sorption follows the removal of volatile matter at various temperatures, as shown in Table XIII. A number of determinations were

TABLE XIII
EFFECT ON SORPTION OF HEATING COMMERCIAL CARBON
BLACK C AT VARIOUS TEMPERATURES

Temp., °C.	Volatile loss, %	x/m , methylene blue per gm. of carbon	Sorption index
20	—	38.8	6.9
600	2.0	38.2	6.4
700	2.1	38.4	6.6
800	4.1	40.0	8.0
1000	7.0	41.6	10.4

made at successively higher temperatures. The increase of sorption depends on the removal of volatile matter, and becomes particularly noticeable at 1000° C. Such temperatures are of the same order of magnitude as those employed in the activation of charcoal, where it was found that temperatures up to 1100° C. may be used with advantage.

Volatile Constituents

Carbon black is by no means pure carbon, as was shown some time ago by Neal and Perrott (10). Various volatile constituents were found to exist in amounts as high as 10% or more of the total weight of the carbon black. More recently, attempts have been made to relate the amount of volatile matter with the rubber reinforcing characteristics of the carbon. Johnson (8) showed that a black with very high volatile content exhibited unsatisfactory behavior in rubber, the reinforcement being low and the cure retarded. In a later publication (9) the same author emphasized the effect of high oxygen content. Neal and Perrott had shown that much of the volatile matter consisted of oxygen, which was removable as carbon monoxide upon heating to high temperatures. Johnson concluded that high volatile content is accompanied by high accelerator sorption. Wiegand and Snyder (19), on the other hand, found the volatile test difficult to employ and unreliable as an indication of vulcanization characteristics.

The samples produced from pyrolysis waste gases under various conditions of channel heights and draft control have been examined. Samples were placed in a platinum crucible and heated to 105° C. to remove water. A tightly fitting lid was placed on the crucible, and the latter after being weighed was placed in an electric furnace at 950° C. for a period of seven minutes, then cooled in a desiccator and weighed.

Discussion of Volatile Determination

Table XIV shows the effect of channel height on the volatile content. Values are highest at small channel settings, falling off to a minimum as channel height is increased. At the greatest channel height there is definite indication of a small increase in volatile content. These results would be predicted because very low channel settings are likely to interfere with the flame in such a way as to favor incomplete combustion, with a consequent increased formation of tars, etc. The slight increase at high channel settings

TABLE XIV
EFFECT OF CHANNEL HEIGHT ON VOLATILE CONTENT

Sample	Channel height, in.	Yield, lb. per 1000 cu. ft.	Modulus at 500% elongation, kg. per sq. cm.	T_B , kg. per sq. cm.	Volatile, %
C29	1.92	3.3	247	296	6.8
C17	2.44	4.4	253	302	5.8
C18	2.84	3.9	244	304	4.6
C19	3.20	3.4	228	285	3.7
C21	3.61	2.2	204	228	5.0

is likely to be caused by the reduction in channel temperature which takes place under these conditions. Further evidence for this conclusion may be found in the results of Drogin (4), who shows that the volatile content of the carbon recovered from the sides of the channel is much greater than that of the carbon removed from the face. The temperature of the sides of the channel is, of course, much lower than that of the face, which is directly in contact with the flames.

Values, obtained from the rubber tests, have been inserted in Table XIV. Some indication of possible correlation exists, in that the lowest volatile content is obtained when the rubber reinforcement is at a maximum. On the other hand, the greatest volatile content appeared at lowest channel settings, but the corresponding rubber reinforcement was not far from the optimum, and the corresponding sorption was very low.

The highly retarded cure and high sorption shown by samples produced at great channel heights are not reflected in the volatile test. It is clear, in the case of carbon black produced in this experimental plant, that the volatile test itself gives little indication of the vulcanization behavior to be expected of the sample.

Restriction of draft has already been shown to exert but a small effect on the tests that have been applied. As shown in Table XV the volatile content exhibits no correlation with this variable.

TABLE XV
EFFECT OF DRAFT CONTROL ON VOLATILE CONTENT

Sample	Draft, %	Yield, lb. per 1000 cu. ft.	Modulus at 500% elongation, kg. per sq. cm.	T_B , kg. per sq. cm.	Volatile, %
C22	100	3.1	235	290	4.0
C23	50	3.2	224	291	5.3
C24	38	3.5	249	311	4.2
C18	27	3.9	244	328	4.6
C25	21	3.5	249	321	6.0

The time during which the sample remains in the channel has a definite effect on the volatile content as would be expected, since the temperature of the channel is of the order of 400° C., which is sufficiently high to destroy most organic compounds, although some of the constituents of the tars probably consist of highly condensed ring systems which are known to be capable of resisting these temperatures. The volatile matter also includes oxygen that is probably present in a chemically combined state. Neal and Perrott found that continued heating at 445° C. removed considerable amounts of carbon monoxide. From both of these points of view longer heating at 400° C. caused by slow channel speed must therefore reduce the volatile

TABLE XVI

EFFECT OF CHANNEL SPEED ON VOLATILE CONTENT

Sample	Time of reversal, sec.	Modulus at 500% elongation, kg. per sq. cm.	T_B , kg. per sq. cm.	Volatile, %
C26	2.4	243	302	4.6
C18	3.9	244	328	4.6
C27	7.6	245	316	3.0

content. Drogin (5), however, mentions that a larger number of burner tips producing higher temperatures in the burner house increases the volatile content. In the present case a reduction is noted, but no relation between this change and rubber reinforcement has appeared, as is shown in Table XVI.

It should be pointed out, however, that none of the samples that were produced in this laboratory exhibited a volatile content as high as that reported by Johnson in the case of certain blacks which behaved badly in rubber. Hence, the tests may be of use in identifying samples with particularly unfavorable properties.

Apparent Density

The apparent density was determined by tapping a known weight of carbon in a graduated cylinder until no further change in volume could be produced. The test is a relative one and may be applied only if the carbons have received identical mechanical treatment, as in the present case.

TABLE XVII

EFFECT OF CHANNEL HEIGHT ON APPARENT DENSITY

Sample	Channel height, in.	Apparent density
C29	1.92	0.079
C17	2.44	0.102
C18	2.84	0.105
C19	3.20	0.109
C21	3.61	0.131

A definite relation between channel height and apparent density has been found in the case of carbon black produced from pyrolysis off-gas. As is shown in Table XVII, the density increases in a regular manner with increase of channel height. This relation is similar to that found with dye sorption, and, therefore, bears the same relation to the rubber test.

Since the true density of all carbon blacks is probably the same, the apparent density may be taken as a measure of the distribution of particle size and of particle shape. It is, therefore, probable that the great channel height produces a larger proportion of fine particles which pack among the larger particles, thus giving a higher apparent density and increased sorption.

Apparent density determinations obtained with black from propane-butane did not produce such regular results, and while the general order was the same, various inversions appeared at intermediate channel heights. Draft control had no effect on the apparent density, while continued heating on the channel produced a sample of high density (0.14).

Conclusions

Channel height is undoubtedly the most important single variable affecting the properties of carbon black produced in an experimental plant under constant flame conditions (*i.e.*, burner tip and gas pressure). Proper adjustment of this variable is essential if the maximum yield of good quality carbon is desired, since rather sharp maxima exist in both yield and quality. The greatest yield is obtainable at channel settings approximately intermediate between the lowest channel height tolerated by the flame and the highest at which any recovery of carbon is possible. The rubber reinforcing properties of the carbon follow the yield, and at all events in the plant under discussion, the most valuable method of gauging quality would be to estimate the yield.

Restriction of the draft increases the yield only if it assists in the production of steadier flames, and when carried to the point of reducing luminosity it reduces the yield. Again the reinforcement of rubber follows the yield insofar as the latter is affected by the draft.

Channel height is one of the most important factors influencing the sorptive power of the carbon. The amount of sorption of methylene blue rapidly increases with channel height, so that the relation between channel height and the logarithm of sorption index is approximately a straight line. This means that in the region of channel heights between the lowest and the one giving maximum yield, both the sorption and rubber reinforcement are increasing. At channel heights above that of maximum yield, however, the situation is reversed, since reinforcement falls off as sorption increases. No general relation may, therefore, exist between sorption and reinforcement.

A consideration of the time of cure required to produce optimum tensile strength indicates that very high channel heights produce very retarded cures, while all other samples cured at almost the same rate. It may be said, with safety, that if the sorption is very great the cure will be retarded.

If the results obtained in an experimental plant may be considered to have general application, it is clear why the sorption test has given such indefinite results in the hands of previous investigators. The reinforcement of rubber is a complex phenomenon in which a number of factors play individual parts. Thus it is possible for two samples of carbon black to differ widely in sorptive power and yet show similar rubber reinforcement.

The volatile content of carbon black changes with channel height in a manner similar to the yield. This test, however, gives even poorer correlation with the rubber properties of the carbon, since the samples produced at high channel heights, and behaving very differently in rubber, contained very little more volatile than the optimum amount.

It is significant that carbon blacks produced from gas mixtures of widely different composition show very similar properties, the important factor in every case (with the same burner tip) being the position of the depositing surface in the flame.

In a small experimental plant it has been possible to vary the yield, sorption, and rubber reinforcing properties of the product. It is well to consider, however, just how closely these results may be related to those that would be obtained in full-scale practice. While the burners and channels were similar to those generally employed, the number and arrangement of the flames were so different that the temperature in the burner house was much lower and, hence, the atmospheric conditions were very dissimilar. It is nevertheless very significant that carbon blacks that exhibit properties so similar to those obtained in commercial plants should have been produced. No drastic differences in the fundamental process of carbon deposition may, therefore, have existed.

Since channel height is the all-important variable, it may be suggested that changes in the quality of carbon black coming from a given plant are due to variations in the effective channel height brought about by atmospheric disturbances and fluctuations in gas pressure. While the sorptive capacity is of little use to the rubber chemist as a test of the quality of an unknown sample, it bears a direct relation to the channel height at which the sample was produced. If determinations could be made rapidly enough, it should be possible to control the conditions in the apparatus by following the sorptive capacity of the carbon being produced at any given time.

Acknowledgment

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A STUDY OF CUPRENE FORMATION¹

By J. M. CALHOUN²

Abstract

The copper oxide catalyzed polymerization of acetylene to cuprene has been studied between 230° and 330° C. by the flow method. The reaction shows an initial induction period at the lower temperatures followed by a rapid rise to a maximum rate and a more gradual decrease. With increase in temperature the induction period becomes shorter, and the maximum rate attained becomes greater. If commenced at 330° C. the reaction is explosive. Analysis of the exit gas shows considerable ethylene and some free hydrogen, the amounts increasing with the temperature of the reaction. This indicates that the hydrogen split off in cuprene formation does not bear a constant ratio to the amount of cuprene formed. The yield of cuprene based on acetylene reacting is about 85% of theory, which is 4 to 10% lower than values based on a volume contraction of acetylene alone.

An exponential equation has been derived which expresses the rate of absorption of acetylene at 290° C. over a period of 72 hr. under the conditions of the experiment. The equation is integrated to give the quantity of acetylene absorbed at any time. This makes a prediction of yields possible. The heat of polymerization was calculated from the determined heat of combustion of cuprene. Various theories regarding the mechanism of formation and structure of cuprene are discussed, and the photochemical evidence of a chain reaction is supported.

Introduction

Cuprene is a substance about which very little is known. It is a light-brown, amorphous, solid, polymerization or condensation product of acetylene that can be prepared in a variety of ways, the most common of which depends on the catalytic action of copper or copper oxide. It was first reported in 1898 by Erdmann and Kothner (6) who passed acetylene over spongy copper at 250° C. They believed cuprene to be a complex copper acetylide, and proposed the formula $C_{44}H_{64}Cu_3$. At temperatures above 400° C. decomposition of the acetylene took place with deposition of carbon black. Alexander (1) a year later claimed that most of the copper could be removed from the cuprene by boiling with dilute acids, and he concluded that it was taken up only mechanically by the cuprene.

In 1900, Gooch and Baldwin (8) obtained cuprene at 225° C. using a cupric oxide catalyst, and from an analysis of the product suggested that cuprene was a mixture of hydrocarbons from $C_{12}H_{10}$ to $C_{16}H_{10}$. Sabatier and Senderens (25, p. 329 *et seq.*; 26) used reduced copper at 180° C. and obtained a formula $(C_7H_8)_n$. The formation of cuprene was accompanied by liquid and gaseous by-products consisting of olefinic and aromatic hydrocarbons. Kaufmann and Schneider (14) in 1922 made a series of combustion analyses of cuprenes obtained with both copper and copper oxide at temperatures of 230° to 250° C. These analyses gave empirical formulas of $C_{11}H_{10}$ to $C_{15}H_{10}$.

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In view of recent evidence regarding the formation and nature of cuprene, none of these formulas can be considered as satisfactory. The only agreement is in the fact that some hydrogen appears to be split off during the polymerization.

The polymerization of acetylene to cuprene has been accomplished by a number of other methods. This indicates that copper is by no means essential to the reaction. Nickel and cobalt at 180° C. cause a very slow formation of cuprene, the major products being liquid and gaseous hydrocarbons (9, p. 172; 25). Increase in temperature causes decomposition and charring. Cuprene is also produced from acetylene by the action of the silent electric discharge (12, 13), a high frequency electro-magnetic field (23), high voltage cathode rays (4, 15, 21), ultra-violet light of a wave-length below 2537 Å (3, 11, 15, 16, 17, 18), mercury photo-sensitization (2, 22), and α -particles from radon (15, 24). Although the cuprenes obtained in many of these cases were present in quantities too small to analyze, the physical appearance and properties of the polymers were the same.

Cuprene is extremely inert. There is no known solvent for it, and it undergoes no chemical reactions except those of such severity that decomposition of the original substance is probable, *e.g.*, it is attacked by strong nitric or sulphuric acid and bromine at 130° C. under pressure (14). Cuprene cannot be sublimed *in vacuo* at 300° C., and at higher temperatures decomposition takes place. It burns slowly in air with a smoky flame. Physically, cuprene varies greatly with the conditions of preparation, and may be loose, soft and flocculent, or hard and comparatively dense. A number of uses for cuprene suggested in the literature are: a cork substitute, an ingredient in plastics, acid resistant and electrical insulation material, an absorbent for liquid explosives, a substitute for charcoal in black powder, etc. (10).

This investigation was undertaken because of the contradictory evidence in the literature concerning cuprene, and the general lack of information regarding the nature of the reaction. It was restricted to a study of the copper catalyzed polymerization by the flow method, the reaction being followed by measuring the rate of disappearance of acetylene at constant pressure under various controlled conditions.

Apparatus

The polymerization was carried out in a reaction chamber consisting of a Pyrex tube 1.25 in. in diameter and 24 in. long. An inlet and an outlet tube and a 360 degree Centigrade thermometer were fastened in the ends with rubber stoppers. A concentric iron pipe wound with nichrome wire and insulated with asbestos served as the heating unit. The 110 volt a-c. with three variable resistances in series was used for temperature control.

In preliminary experiments wet meters were used to measure the input and output of acetylene. However, even after careful calibration against a standard volume, they were found insufficiently accurate for the low rates of flow necessary. Two devices were then constructed to measure the volume of gas passed in and out of the reaction chamber.

Iron pipes 2 in. in diameter and 22 in. long were welded at both ends and fitted with $\frac{1}{4}$ in. pipe for the necessary connections. Two glass gauges were attached to each tank. The first gauge was a 50 cc. burette, which was connected to the tank at both top and bottom. The second gauge was connected to the tank at the bottom only, the top being left open to the atmosphere. Mercury reservoirs constructed of sheet iron were connected at the bottom to each tank by pressure tubing. A T-tube fitted with needle valves at the top of each reservoir provided an inlet and escape for compressed air. Each tank was connected to the system at the top through a three-way stop-cock.

By applying air pressure to the reservoir, the mercury could be raised in the tank and in the glass gauges. When the level in both gauges was the same, the pressure in the tank was atmospheric. Each tank was calibrated with water so that the volume could be read from the graduated gauge. The tanks had a capacity of about 1200 cc., and the volume could be measured to within 1 cc.

The complete set-up is shown in Fig. 1. The acetylene, although 99% pure, was first passed through a purification train consisting of sulphuric acid to remove traces of phosphine, active carbon to remove organic sulphur

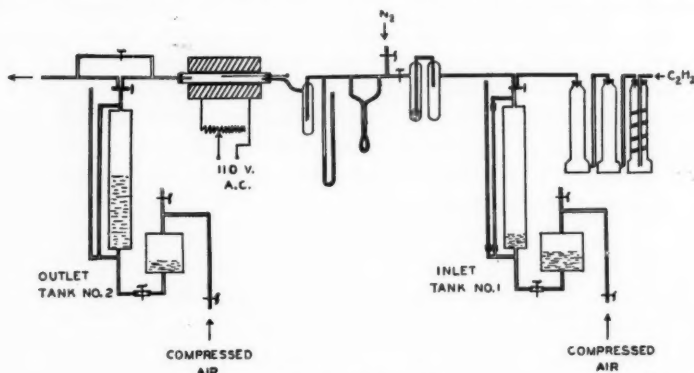


FIG. 1. Apparatus.

compounds, and soda lime for drying. After tank No. 1 was placed a bubbler, a flowmeter and a manometer, all containing oil and protected at each end by traps. A T-tube next to the flowmeter and a by-pass around tank No. 2 permitted flushing of the system with nitrogen.

At the beginning of a run, tank No. 1 was filled with acetylene and tank No. 2 with mercury. The catalyst, finely divided cupric oxide, was spread evenly on an aluminium foil carrier 15 by 5 cm. bent in a half cylinder and placed inside the reaction tube. The system was then completely flushed out with nitrogen. When the desired temperature was reached, the by-pass was closed and acetylene forced steadily from tank No. 1 to tank No. 2 under a slight positive pressure (about 1 cm. mercury). The rate of gas flow during

each run was made roughly double the rate of absorption in order that any by-products might be carried away from the reaction zone. The gas volume in both tanks was read at regular intervals, the pressure in the system being momentarily reduced to atmospheric. The apparatus was so designed that each tank could be filled or emptied independently of the system without interruption of the run. At the completion of the run the by-pass was opened, and the system again flushed with nitrogen. After cooling to room temperature the cuprene was removed and weighed.

Experimental Results

The Effect of Temperature on Cuprene Formation

A series of runs was made at different temperatures, using the same initial weight of catalyst but operating for different lengths of time. The cuprene formed as a spongy mass on the carrier, and, when removed, the catalyst was no longer visible. Small amounts of a greenish oil collected at the cooler end of the reaction tube. This oil was no doubt a mixture of aromatic and olefinic hydrocarbons as reported by Schl pfer and Stadler (27).

Table I shows the extremely rapid increase in the rate of cuprene formation with increase in temperature. The average yield of cuprene per hour per gram of copper increases from 2.89 gm. at 230° C. to 89.3 gm. at 310° C.

TABLE I
THE EFFECT OF TEMPERATURE ON THE YIELD OF CUPRENE

Run No.	11	7	8	16	15
Temp., °C.	230	250	270	280	310
Time, hr.	8	7	6	5	2
Rate of input flow, litres per hr.	0.25	0.5	0.75	1.5	3.0
Volume C ₂ H ₂ absorbed, N.T.P., litres	0.475	1.340	2.020	3.040	3.260
Yield of cuprene, gm.	0.462	1.397	2.116	3.253	3.573
Average yield of cuprene per hr., per gm. of copper	2.89	9.97	17.6	32.5	89.3
*Apparent yield of cuprene, % theory	80.3	88.5	89.4	91.6	93.8
Copper content calculated, %	4.33	1.43	0.94	0.61	0.56
Copper content by ignition, %	3.60	1.17	0.69	0.80	0.52

*NOTE:—The apparent yield of cuprene as per cent of the theoretical yield is calculated from the volume contraction of acetylene and from an empirical formula of (C₂H₂)_n for cuprene. The errors involved in such a calculation are discussed after the section on gas analysis.

Weight of CuO used, 0.0250 gm.

The rate of cuprene formation is not uniform with time, so that the average yield per hour gives only a rough comparison, but is sufficient to show the important effect of temperature. At 230° C. the reaction is relatively very slow and the cuprene formed is rich in copper, and is loose and fluffy with almost no coherent qualities. It is brown, becoming lighter as the reaction proceeds and the copper content is reduced. Only at temperatures above 300° C. does the cuprene become darker.

The discrepancy between the calculated and analytical values for the copper content is due to the fact that some of the catalyst may remain on the carrier, while the balance is not necessarily evenly distributed throughout the cuprene.

The increase in the apparent yield of cuprene as per cent of the theoretical yield from 80.3% at 230° C. to 93.8% at 310° C. is quite striking. It can be due only to a difference in the proportion of oily by-products or tar formed to that of cuprene. Therefore the temperature coefficient for tar formation must be less than that for cuprene formation. In addition it may be observed (Table I) that the rate of gas flow was made greater at the higher temperatures to accommodate the more rapid formation of cuprene. That is, the time of contact of acetylene not polymerized to cuprene was less, and the quantity of by-products formed would be relatively smaller.

A clearer picture of what is happening is given by the rate of absorption of acetylene during each run (Table II). The times correspond to the mid-points in the time intervals over which the absorption was measured. This measurement does not distinguish between solid and liquid polymerization products, but since cuprene represents by far the largest portion, the rate of absorption of acetylene may be considered as a measure of the rate of cuprene formation.

TABLE II
THE EFFECT OF TEMPERATURE ON THE RATE OF ABSORPTION OF THE ACETYLENE

Run No.	11		7		8		16		15	
Temp., °C.	230		250		270		280		310	
	Time	Rate of absorption	Time	Rate of absorption	Time	Rate of absorption	Time	Rate of absorption	Time	Rate of absorption
	1.0	0.5	0.25	1.6	0.25	18.0	0.125	27.6	0.167	111.6
	2.0	0.3	0.75	2.2	0.75	25.4	0.375	48.8	0.5	100.5
	3.0	0.2	1.25	13.4	1.25	25.8	1.0	42.1	0.833	92.4
	3.75	1.0	2.0	14.5	2.0	22.8	2.0	35.3	1.25	80.8
	4.25	0.9	3.0	12.9	3.0	19.1	3.0	30.5	1.75	72.6
	4.75	5.2	4.0	11.9	4.0	15.0	4.0	27.0		
	5.25	7.5	5.0	10.5	5.0	12.7	4.75	24.0		
	5.75	9.2	6.0	9.8	5.75	11.6				
	6.25	6.0	6.75	9.6						
	7.00	6.3								
	7.75	6.2								

NOTE:—Time in hours; rate of absorption of acetylene in litres per hour per gram of copper, measured at 25° C., 760 mm.

The data are plotted in Fig. 2, which illustrates several striking features. There is an initial induction period for the reaction, followed by a rapid rise to a maximum rate and a more gradual decrease. With increase in temperature the induction period becomes shorter and the maximum rate attained becomes greater. Above 280° C. the rate of absorption of acetylene is already

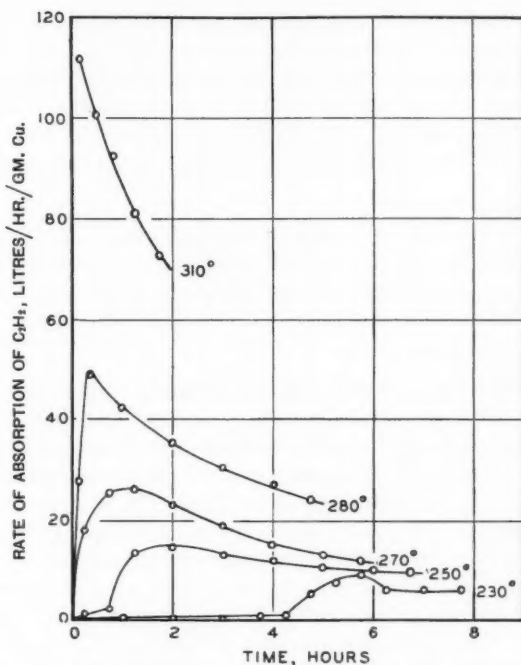


FIG. 2. Effect of temperature on rate of absorption of acetylene.

below the maximum before the first reading can be taken. An interpretation of this behavior will be left for a later section. It may be noted that the area beneath the rate curves corresponds to the quantity of cuprene formed, and explains the great effect of temperature on yield.

Two attempts to operate at 330° C. resulted in small explosions with an immediate deposit of carbon black throughout the apparatus. However, if a run was begun at 290° C. and the temperature raised gradually to 330° C., or even higher, no explosion occurred. The explanation for this can be found in Fig. 3, which shows the maximum rate of absorption attained (the peaks of the curves in Fig. 2) plotted against temperature.

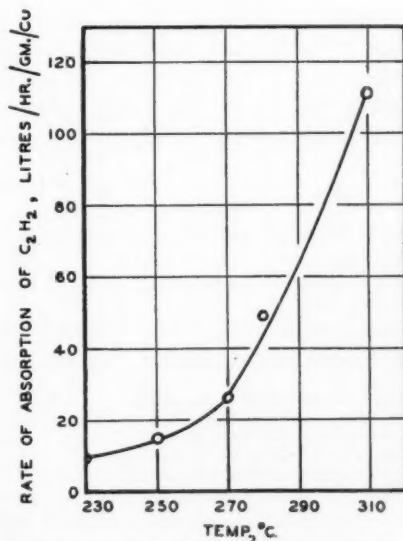


FIG. 3. Maximum rate of absorption of acetylene.

The maximum rate, which for practical purposes is the initial rate at high temperatures, increases very rapidly, and at 330° C. is so great that the exothermic nature of the reaction causes a sudden further elevation of temperature resulting in decomposition of the acetylene and deposition of carbon black. If, however, the reaction is initiated at 290° C. the rate is well below the maximum before 330° C. is reached, and no explosion occurs.

Analysis of the Exit Gas

An analysis of the exit gas in several runs was made, since the identification of gaseous by-products might throw some light on the nature of the reaction. If cuprene contains less hydrogen than acetylene as claimed in the literature, the hydrogen split off should be present in the by-products either free or combined with excess acetylene.

Three runs were made at different temperatures to collect samples of the exit gas. The quantities of catalyst and rates of gas flow were chosen to give large amounts of cuprene and a high concentration of impurities (if any) in the exit gas. At the close of each run, the reaction tube was flushed with acetylene to collect all the impurities in tank No. 2, from which two gas samples were taken. The gas was analyzed in duplicate in an Orsat apparatus. Since it was essential to distinguish quantitatively between acetylene and ethylene, ammonium cuprous chloride reagent was unsatisfactory. Absorption in fuming sulphuric acid gave the total unsaturates. Acetylene was then estimated on a separate sample by absorption in neutral silver nitrate solution and titration of the nitric acid liberated. Ethylene does not interfere, and was obtained by difference.

Table III gives the data for each run and Table IV the analysis of the exit gas. The amount of nitrogen is higher than that expected, although small amounts may be present in the acetylene and the ratio of input gas to exit gas is from four- to sevenfold. The apparatus was found to be free from air leaks which would be improbable with the system under a positive pressure.

TABLE III
PREPARATION OF CUPRENE FOR COLLECTION OF EXIT GAS

Run No.	27	25	26
Temp. ° C.	245-255	280-300	330-350*
Weight of CuO used, gm.	0.0531	0.0526	0.0464
Time, hr.	4.383	2.500	2.167
Rate of input flow, litres per hr.	1.0	2.5	2.9
Volume of gas input, litres	3.636	5.599	5.570
Volume of gas output, litres	0.906	0.815	0.956
Apparent contraction, litres	2.730	4.784	4.614
Yield of cuprene less copper, gm.	2.80	5.12	4.88
Apparent yield of cuprene, % theory	88.6	92.1	90.9

Reaction started at 290° C. to prevent explosion. Temperature raised to 330° C. in 20 min.

*NOTE:—All gas volumes at N.T.P.

TABLE IV
ANALYSIS OF EXIT GAS

Run No.	27		25		26	
Temp. ° C.	245-255		280-300		330-350	
CO ₂	0.8	0.8	0.5	0.1	0.4	0.1
O ₂	0.8	0.6			1.2	0.7
C ₂ H ₂	75.0	74.7	47.8	48.2	26.8	26.1
C ₂ H ₄	12.5	12.8	35.1	34.8	46.0	47.0
C ₂ H ₆	0.0	0.2	0.3	0.3	0.5	0.7
H ₂	1.5	0.3	3.0	3.0	7.9	6.8
N ₂	9.4	10.6	13.3	13.6	17.2	18.6

The most interesting feature is the large amount of ethylene produced, which together with some free hydrogen and traces of ethane all increase with the reaction temperature. It is believed that the hydrogen is split off from the cuprene after the acetylene is polymerized, and that such an elimination is not essential to the mechanism of the reaction. Ethylene and ethane are then formed by the catalytic hydrogenation of excess acetylene. The yields are calculated on this basis and given in Table V.

TABLE V
CALCULATION OF YIELDS

Run No.	27	25	26
Temp., °C.	245-255	280-300	330-350
Products recovered, litres:			
C ₂ H ₂ polymerized to cuprene	2.412	4.410	4.204
C ₂ H ₄	0.115	0.285	0.444
C ₂ H ₆	0.001	0.002	0.006
H ₂	0.008	0.024	0.071
True contraction, litres	2.738	4.808	4.685
Total C ₂ H ₂ reacted, litres	2.854	5.095	5.135
Yields, % by volume of C ₂ H ₂ reacted:			
C ₂ H ₂ polymerized to cuprene	84.5	86.5	81.8
C ₂ H ₄	4.03	5.60	8.65
C ₂ H ₆	0.03	0.05	0.12
Tar (by difference)	11.4	7.8	9.4
Free H ₂	0.28	0.48	1.38
Total H ₂ split off:			
% by volume of C ₂ H ₂ reacted	4.37	6.18	10.27
% by weight of C ₂ H ₂ polymerized to cuprene	0.40	0.55	0.96

The quantity of each impurity was determined from the volume of exit gas and its average composition. Since free hydrogen represents an increase in volume, this amount was added to the apparent contraction to give the true

contraction of acetylene. Ethylene and ethane represent no volume change, but must be added to the true contraction to give the total acetylene reacted. The yields of each product are then calculated on this basis. The total hydrogen split off equals the free hydrogen, plus the ethylene, plus two times the ethane. This does not take into account the tar, which may be hydrogenated to a slightly greater or smaller degree than is acetylene.

If the elimination of hydrogen were an essential step in the polymerization, one would expect a constant proportion of carbon to hydrogen in cuprene, irrespective of the conditions of preparation. This is not the case. Combustion analyses of cuprenes prepared by Kaufmann and Schneider (14) at 230-240° C. gave percentages of hydrogen varying from 5.25 to 6.88. The theoretical amount in acetylene is 7.74%, and therefore a loss of 0.86 to 2.49% occurred. Table V shows that the elimination of hydrogen from the cuprene prepared by the writer amounted to only 0.40% at 245-255° and 0.96% at 330-350° C. Therefore such formulas as $(C_7H_8)_n$ and $(C_{15}H_{10})_n$ proposed for cuprene in the literature are not applicable.

Photochemical evidence, referred to later, shows that cuprene corresponding to $(C_2H_2)_n$ has been prepared, and that either no free hydrogen was found, or that it was observed only after the polymerization was completed (15, 19). It is, therefore, suggested that hydrogen is split off by slight thermal decomposition of the cuprene itself after polymerization, and not by an elimination essential to the mechanism of the reaction. Additional evidence for this is in the fact that the amount of hydrogen split off increases with the reaction temperature, and that cuprene is known to be thermally unstable even when heated in an inert atmosphere.

That the formation of hydrogen and ethylene could be due to the decomposition of acetylene, entirely independent of cuprene formation, is not impossible. This, however, would involve the deposition of carbon black which was not observed under the conditions of the experiment, either on the walls of the reaction chamber or upon examination of the cuprene under a microscope. It is believed that the evidence of combustion analyses reported in the literature, the instability of cuprene, and the fact that no carbon black could be found, favors the reactions as outlined. In any case it does not affect the conclusions drawn regarding the formation of cuprene itself, and the error involved in the calculation of theoretical yields would be small.

The difference between the apparent yield of cuprene determined by a volume contraction alone and the true yield as calculated above is considerable. All yields of cuprene reported in the literature and based on a volume contraction of acetylene are too high by as much as 4 to 10%. The apparent yields of cuprene are still, of course, comparable. Any error involved in the use of the empirical formula $(C_2H_2)_n$ for cuprene for the calculation of yields is negligible because of the small amount of hydrogen removed. The yield of tar, as shown in Table V, is greatest at the lowest temperature. This again is largely due to the decreased rate of gas flow and the longer time of contact of the acetylene. At 280° to 300° C. the yield of tar is least, and at 330° to

350° C. it is again somewhat greater, owing probably to the extreme of temperature, since the time of contact is roughly the same.

It is interesting to note that Fischer and Peters (7) prepared cuprene in a liquid medium and obtained yields similar to the above. Copper was deposited on kieselguhr and suspended in methyl naphthalene. The reaction was carried out in the presence of hydrogen at 230° C.; 86.1% of the acetylene was recovered as cuprene and 12.4% as ethylene. The excess of hydrogen would account for the larger proportion of ethylene.

An Equation for the Rate of Absorption of Acetylene in Cuprene Formation

It was observed that many of the rate curves for the absorption of acetylene in cuprene formation at the higher temperatures appeared to be of the exponential type. A run was therefore made over a long period of time to obtain as accurate data as possible for a mathematical analysis of the curve. If an equation could be established it would be very useful for the prediction of rates and yields, and might in addition prove of theoretical interest.

The data and calculations are given in Table VI. After 32 hr. running, the reaction was continued for another 40 hr. without supervision. During

TABLE VI
THE RATE OF ABSORPTION OF ACETYLENE DURING CUPRENE FORMATION

<i>t</i>	<i>y</i> (experimental)	y_1 $31.1e^{-0.0225t}$	y_2 $14.7e^{-0.222t}$	y_3 $45.4e^{-1.125t}$	$y_1 + y_2 + y_3 = y$ (calcd.)
0.05	105	31.0	14.6	42.8	88.4
0.15	91	30.9	14.2	38.2	83.3
0.3	81.5	30.8	13.8	32.2	76.8
0.5	70.0	30.6	13.2	25.8	69.6
0.8	61.5	30.3	12.3	18.3	60.9
1.25	50.8	29.8	11.1	11.0	51.9
1.75	47.2	29.4	10.0	6.2	45.6
2.5	39.2	28.7	8.5	2.7	39.9
3.5	34.2	27.8	6.7	0.8	35.3
4.5	32.3	26.9	5.4	0.3	32.6
5.5	31.0	26.0	4.3		30.3
7.0	28.3	24.8	3.1		27.9
9.0	24.9	23.2	2.0		25.2
11.0	23.3	21.8	1.3		23.1
13.0	22.1	20.4	0.8		21.2
15.0	18.9	19.1	0.5		19.6
17.0	17.7	17.9	0.3		18.2
19.0	16.8	16.8	0.2		17.0
20.5	16.0	16.0	0.1		16.1
23.0	14.2	14.7			14.7
25.0	13.3	13.7			13.7
27.0	12.9	12.9			12.9
29.0	13.0	12.1			12.1
31.0	11.0	11.4			11.4
49.0	4.7	6.3			6.3
72.5	3.2	3.0			3.0
100.0		1.2			1.2
200.0		0.05			0.05

Run No. 78; temp., 290° C.; weight of CuO used, 0.0125 gm.; *t* = time, hr.; *y* = rate of absorption of acetylene, litres per hr. per gm. copper at 25° C., 760 mm.

this time the temperature varied somewhat, but it was held constant at 290° C. for a period of one hour for each reading. This would not cause much error at the lower end of the curve, since we were interested in the rate of absorption, rather than in the quantity of acetylene absorbed. In Column 1, Table VI, the time in hours, t , corresponds to the midpoint of the interval over which the absorption was measured. Column 2 shows the experimentally determined rate of absorption of acetylene, y , measured in litres per hour per gram of copper at 25° C., 760 mm.

The equation for the rate curve was determined as follows. Fig. 4 shows a plot of $(\log y, t)$, the values of y being taken from the smoothed experimental rate curve. It is seen that for $t > 17$ a straight line is obtained, and the

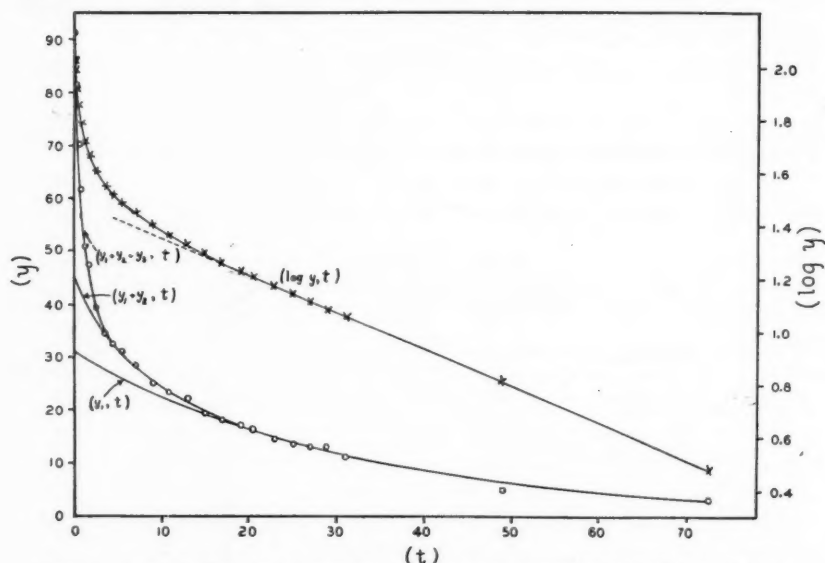


FIG. 4. Rate of absorption of acetylene during cuprene formation at 290° (run No. 78).
 $y_1 = 31.1e^{-0.0325t}$; $y_2 = 14.7e^{-0.222t}$; $y_3 = 45.4e^{-1.135t}$.

equation of this portion of the curve is therefore of the type, $y = ae^{bt}$, where a and b are constants. The constants are evaluated by the method of averages. This gives the equation:

$$y_1 = 31.1e^{-0.0325t} \quad (1)$$

Values of y are then calculated for $t < 17$, and the difference between the calculated and experimental values of y is plotted against t . An equation of this difference curve is obtained in a manner similar to that adopted before. This makes the equation valid for $t > 4.5$.

A second difference curve for $t < 4.5$ is obtained by repeating the process. This gives as the final equation for run No. 78:

$$y = 31.1e^{-0.0325t} + 14.7e^{-0.222t} + 45.4e^{-1.135t}, \quad (2)$$

which is valid for all values of $t > 0.3$.

Table VI shows the calculated values for each term of the equation (Columns 3, 4, 5) which are summed in Column 6. A comparison of the calculated and experimental values for $t > 0.3$ shows good agreement. This is borne out in Fig. 4, which shows how close the experimental points come to the calculated curve. An extrapolation of the curve is of interest, although the validity of the equation is not certain much beyond the experimental values.

Equation (2) can be integrated to give the total quantity of acetylene absorbed, x (litres per gram of copper at 25° C., 760 mm.) at any time, t :—

$$x = 1066 - 957e^{-0.0325t} - 66.2e^{-0.222t} - 40.0e^{-1.135t} \quad (3)$$

The constant of integration is found by substituting experimental values of x and t . A few experimental and calculated values are compared in Table VII, and it is seen that the agreement is very good. The average error for 38 values is only 0.5%.

The extrapolated values show very clearly how the reaction slows up. The equation would predict a limiting value of $x = 1066$ at infinite time, but this is not necessarily true. The volume of acetylene absorbed may be converted readily to grams of cuprene, if an apparent yield of, say 90%, is assumed. A calculation of the copper content of the cuprene at various stages based on this value is given in the last column of Table VII. It is seen that 0.1% copper appears to be about the minimum obtainable under the conditions of the experiment.

TABLE VII
THE QUANTITY OF ACETYLENE ABSORBED DURING
CUPRENE FORMATION.

t	x (exptl.)	x (calcd. from Equation (3))	Copper in cuprene, calcd., %
0.4	35.9	35.4	2.9
1.0	74.5	74	1.4
2.0	123.5	123	0.85
4.0	196.9	198	0.52
6.0	260.2	262	0.40
8.0	316.9	317	0.33
10.0	360.7	367	0.28
15.0	475.9	476	0.22
20.0	563.6	565	0.18
25.0	637.3	641	0.16
30.0	702.0	705	0.15
49.0		871	0.12
72.5		975	0.11
100		1029	0.10
200		1065	0.097
1000		1066	0.097

NOTE:—Run No. 78; t = time, hr.; x = total volume of acetylene absorbed, litres per gm. of copper at 25° C., 760 mm.

Any theoretical interpretation of the above equation at the present time would be difficult if not impossible, because of the complicated nature of the reaction. In addition to possible kinetic factors, the rate is influenced by mechanical factors such as the enclosure of the catalyst within the cuprene, decrease in surface as the cuprene builds up in the cylindrical tube, and diffusion of the acetylene through the cuprene. A further complication is caused by side reactions and tar formation.

The chief value of such an equation would be to predict rates and yields. The constants of course will vary with the experimental conditions, but the

available data indicate that an exponential equation is generally applicable, the number of terms depending on the range and accuracy desired. At temperatures at which the induction period becomes appreciable, this would have to be taken into account in the equation.

The Heat of Combustion of Cuprene

The heat of combustion of several samples of cuprene was obtained through the courtesy of Dr. O. J. Walker, University of Alberta. The results are given in Table VIII. Since the heat of combustion of acetylene is approximately 312 kcal. per mole, the heat of polymerization may be calculated and is found to be 61 to 70 kcal. per mole of acetylene polymerized. This shows the strongly exothermic nature of the reaction.

TABLE VIII
THE HEAT OF COMBUSTION OF CUPRENE

	Run No.		
	19	21	78
Temp., °C.	290	290	290
Time, hr.	5	5	72
Copper content, calcd., %	0.50	0.47	0.09
Heat of combustion, cal./gm.	9396 9224 9307	9320 9311	9635 9673
Average	9309	9315	9654

In a paper published since this work was completed, Lind (19) states that α -ray cuprene undergoes spontaneous oxidation in air at room temperature which is nearly complete in 12 or 15 days. He found the heat of combustion of unoxidized cuprene to be 10,203.7 cal. per gm. and that of oxidized cuprene, 7,113.5 cal. per gm. compared with the above values of 9300 to 9600. Lind also calculated for unoxidized cuprene a heat of polymerization of 47 kcal. per mole of acetylene. The calorimetric determinations reported in Table VIII were made six months after the preparation of the cuprene, when any oxidation would presumably be complete. This might account for the discrepancy in the values for the heat of combustion and the rather high heat of polymerization.

Discussion

The polymerization of acetylene to cuprene is of such a complex nature that it is difficult to theorize regarding the mechanism of formation and structure of the polymer. However, various theories proposed in the literature will be discussed in the light of the evidence obtained here, and a possible explanation offered.

Cuprene is chemically almost inert, and there is no known solvent for it. It does not swell as do rubber and cellulose in suitable agents, and it cannot be sublimed *in vacuo*. In fact, all the properties of cuprene indicate a substance of such complexity that no simple formula can be entertained. Its molecular weight must be extremely high, or rather it is in the range where molecular weights become meaningless.

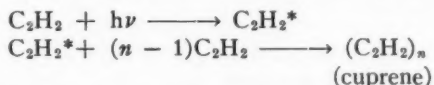
Sabatier and Senderens (26) first suggested that copper formed an unstable acetylide capable of reacting with additional acetylene to give a condensed molecule:



The equations are based on his formula for cuprene, which cannot be considered valid because of the varying proportions of hydrogen to carbon found. Sabatier claims that the regenerated copper reacts indefinitely, while the hydrogen set free combines with unused acetylene to give ethylene.

The photochemical polymerization of acetylene yields more information regarding this reaction. Under the action of α -particles or cathode rays, ionization first takes place, and Lind (15) claims that 20 molecules of acetylene are polymerized for every pair of ions produced. Lind was unable to find a solvent for the polymer, and X-ray examination gave no clue to its structure. He also observed that free hydrogen was produced *after* most of the acetylene was polymerized, owing to bombardment of the cuprene by α -particles. The total amount of hydrogen liberated was only 2% of the acetylene polymerized. This indicated that the formula $(\text{C}_7\text{H}_6)_n$ of Sabatier and Senderens could not apply. However the molecular weight of cuprene must be many times greater than $(\text{C}_2\text{H}_2)_{20}$. In a later paper Lind (20) states that no hydrogen is produced by an electric discharge on a wall skin of cuprene in many hours.

Bates and Taylor (2) in 1927 studied the polymerization of acetylene by ultra-violet light, and proposed a mechanism based on an activation of acetylene molecules by the absorption of a quantum of energy:



The activated acetylene molecules then add on additional acetylene by a chain mechanism.

Melville (22), studying the mercury photosensitized polymerization of acetylene, found no secondary reactions such as the elimination of hydrogen. He concluded that an excited mercury atom on collision with an acetylene molecule formed a complex of the acetylide type, then adding on additional acetylene by a chain mechanism. His calculations indicated a chain length of 10 at 20° and 100 at 250° C., but since the polymer was not volatile at 300° *in vacuo*, he concluded that a secondary polymerization of the products of the gaseous chain reaction took place.

Dostal and Mark (5) have shown that the polymerization of many unsaturated substances is a chain reaction. It is believed that some such mechanism is the most probable explanation for the formation of cuprene. Stepwise addition of acetylene molecules with a shift of hydrogen atoms would be too slow and would yield only low polymers. The fact that no low polymers are found, and that cuprene is formed in the first few seconds of reaction, is strong evidence for a chain mechanism. The following outline conforms to the findings of a recent symposium on polymerization and condensation.*

The initiation of chains is brought about by the collision of two acetylene molecules to form a nucleus. This requires activation by photochemical, thermal or catalytic means which may occur mono- or bimolecularly. In the case of the catalyzed reaction, the copper probably forms an intermediate compound of the acetylide type, and is later eliminated. Evidence for this is found in the fact that the copper becomes distributed throughout the cuprene. The nucleus then reacts with additional acetylene molecules, and this results in growth of the polymer. The energy of activation of this reaction is usually lower than that required for the initiation of chains, so that chain growth can be more rapid than the formation of nuclei. This explains the preliminary induction period observed at lower temperatures, and is characteristic of chain reactions. Increase in temperature shortens the induction period, until, at 330° C., the reaction becomes explosive, another characteristic of chain reactions.

The rate of polymerization by a chain reaction depends on the relative rates of initiation, propagation and termination of chains. As the length of the chains increases, the number of active points at which another acetylene molecule can add becomes smaller. The exponential decrease in rate of cuprene formation observed may be due to this increasing steric factor as the chains become longer, plus such mechanical effects as have already been discussed. However, since cuprene is not deposited throughout the reaction chamber; but grows only on the catalyst carrier, the reaction is not homogeneous but probably occurs in the solid phase. Acetylene molecules will then have to diffuse farther into the cuprene as reaction continues, and the over-all rate may be governed by a diffusion process.

Termination of the chains may be brought about by collisions with the growing polymer of a kind different from that responsible for propagation. If the nuclei still contain double bonds, these may be reduced by thermal or catalytic means, and the valencies set free are used for linking chains together to give a two or three dimensional lattice. The product so obtained has properties quite different from those of ordinary chain polymers, especially in regard to solubility, melting point, and elasticity. That such a secondary polymerization or condensation occurs is shown by the fact that a linear chain of even 5000 chain atoms will swell strongly in suitable solvents and form highly viscous solutions. No such solvent has ever been found for cuprene, and only cross-linkages and a lattice structure can account for its behavior.

*"The phenomena of polymerization and condensation". (A general discussion held by the Faraday Society). Gurney and Jackson, London. 1935.

The above explanation accounts equally well for the formation of cuprene by all the diverse methods. Small amounts of hydrogen are undoubtedly split off, but this is believed to be due to thermal decomposition after polymerization and not to an elimination fundamental to the mechanism of the reaction, as was previously mentioned. In the case of cuprene prepared by some methods, free hydrogen is either entirely lacking or is observed after the acetylene is polymerized. When hydrogen is split off, it combines with excess acetylene to form ethylene. Thus the most recent evidence favors a basic empirical formula for cuprene of $(C_2H_2)_n$ and a structure of extreme complexity.

Acknowledgments

The writer wishes to express his thanks to Shawinigan Chemicals Limited for permission to publish this paper, and to the Director of Plant Research, Mr. A. F. G. Cadenhead, and to members of the department, particularly Mr. A. H. Andersen, Mr. C. Kaufmann and Mr. W. F. Archibald, for many valuable suggestions during this work.

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THE HEAT CONTENT OF WATER SORBED ON CELLULOSE¹

By J. H. SHIPLEY², W. BOYD CAMPBELL³ AND O. MAASS⁴

Abstract

The specific heat of cellulose has been determined for the temperature range -70° to 25° C. The heat capacity of water sorbed to the extent of 5.92 and 12.0% by cellulose has been determined for the range -78.5° to 25° C. These data are compared with the heat capacity of pure water for the same range of temperature, *vis.*, -78.5° to 25° C.

Introduction

The system cellulose-water has been intensively studied in this laboratory. Adsorption and desorption isothermals, the dielectric constants of adsorbed water vapor, the density of adsorbed water, and the heats of wetting at various stages of water adsorption are being studied (1, 2, 5, 6). The objective of this work is to establish a better understanding of the mechanism of water adsorption and of the physical structure of cellulose.

The present paper is a preliminary one on the measurement of the specific heat of cellulose and of the specific heats of water adsorbed to the extent of 6 and 12%. These measurements were made for the range -78° to 25° C., since a comparison can be made with the heat content of free water for this range as determined by Barnes and Maass (4).

Apparatus

An adiabatic, radiation-thermocouple calorimeter as described by Barnes and Maass (3) was employed. Owing to the difficulty in compacting cellulose, with the consequent relatively small volume-heat capacity as compared to that of free water, a small inner calorimeter containing 175 gm. of water was used. The thermal-galvanometer system was arranged to give a sensitivity of 0.0002° C., and the outer bath could be controlled to within 0.001° C. of the temperature of the calorimeter for definite periods. The monel metal container for the cellulose was that used by Hampton and Mennie (8) in their investigation on gelatine.

Procedure

The cellulose was purified from absorbent cotton by treatment with sodium hydroxide and acetic acid in the manner described in detail by Argue and Maass (1).

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This "standard" cellulose was introduced into the clean, weighed, monel metal container, which was then placed in an electric oven for 10 hr., the temperature being maintained at 100° C. Meanwhile, air, dried over concentrated sulphuric acid and phosphorus pentoxide, was passed through the cellulose by means of a hypodermic needle reaching to the bottom of the container. While still in the oven the cover was attached, and, after cooling, the container plus the dry cellulose was weighed. It was found that this weight could be duplicated after the cellulose readsorbed water and then was dried again under the above conditions. This showed that the cellulose was rendered bone-dry by such treatment.

The filled container was prepared for immersion in the calorimeter by suspending it from a cork by a thread of the proper length and placing it in a closely fitting copper tube. Two discs, one of cardboard and the other of copper, were placed above the container inside the copper tube to prevent convection currents, and a piece of adsorbent cotton was placed just below the cork to prevent moisture from creeping into the tube and condensing on the container. Adhesive tape was wrapped tightly around the cork and the top of the tube to prevent the entrance of moisture.

The tube with the container was placed in the requisite cooling bath to bring the container to the required initial temperature. For a temperature of -78.5° C. solid carbon dioxide moistened with acetone was used, while for -38.5° C. and -6.25° C. a bath of ether, stirred by means of a current of air, was used. The bath was maintained at the proper temperature to within $\pm 0.1^\circ$ C. by dropping, from time to time, small pieces of solid carbon dioxide into the ether bath.

In the meantime the calorimeter was assembled as described by Barnes and Maass (3). About 175 gm. of water was introduced into the inner vessel from a weight pipette. The two baths were then brought to thermal equilibrium at the proper temperature, and the temperature was read every five minutes, the deflection of the galvanometer being kept at zero. This was done for 15 to 20 min. to determine the initial temperature of the calorimeter.

The container was then quickly lifted out of the copper tube and lowered into the calorimeter. The transfer took about two to three seconds, and the time at which it was effected was noted exactly. The fall in temperature was followed by running ice cold water into the outer bath, and keeping the two baths in thermal equilibrium as closely as possible. The temperature was recorded until a uniform change took place. This indicated the final temperature.

Water was introduced into the cellulose to the required percentage by means of steam and was accurately determined by weighing the container before and after adsorption.

Although the adsorbed water contributes only from 3 to 7% of the total heat effect, the error introduced was not as large as would at first be apparent. The largest error was a systematic one, and was due to heat gained by the

container when it was transferred from the initial cold bath to the calorimeter. Since this transfer was effected in the same manner and time and under approximately identical conditions for all the experiments, the error so introduced would tend to cancel out when the values for the total heat gained by the container plus cellulose are subtracted from the values for the container plus cellulose plus water to give the heat content of the sorbed water.

In all cases the heat capacities were corrected to a final temperature of 25.00° C.

Results

In Table I are given the total heats of the container and contents between the initial temperatures given in Column 1 and the final temperature. Each one is the mean of at least three determinations. In the case of the empty con-

TABLE I
TOTAL HEATS (CALORIES) GIVEN UP BY CALORIMETER CORRECTED TO FINAL TEMPERATURE, 25.00° C.

Initial temp., °C.	"Standard" cellulose	5.92% water	12.0% water	Empty container
-78.5	695.1	716.8	745.3	601.7
-38.5	439.9	452.0	472.9	371.0*
-25.0				298.7
- 6.25	222.3	229.9	238.3	183.2*

*Calculated values.

tainer, determinations were made from only two initial temperatures as the heat content varied continuously with the temperature. The container was made up of 59.121 gm. of monel metal and 3.068 gm. of lead. Allowing for the specific heat of lead, the specific heat of monel metal agrees with the values obtained by Horn (9) when these are extrapolated to the lower temperatures. Since the major error involved is due to heat gained by the container during transfer, this would appear in the specific heat of the container and not in that of the cellulose.

The heat content (Table II) of the "standard" cellulose is obtained by subtracting the heat content of the container from that of the container plus cellulose. The heat contents of the "5.92%" water and the "12.0%" water, per gram of water, given in Table II, were obtained by subtracting the values

TABLE II
TOTAL HEATS (CALORIES) PER GRAM OF MATERIAL CORRECTED TO FINAL TEMPERATURE, 25.00° C.

Initial temp., °C.	"Standard" cellulose	5.92% water	12.0% water	Free water
-78.5	23.5	92.0	105.0	138.2
-38.5	17.3	51.6	69.0	122.5
- 6.25	9.8	32.3	33.6	107.5

given in Column 2 from Columns 3 and 4 (Table I) respectively, and then recalculating on the basis of one gram of water. The last column in Table II gives the total heats of one gram of free water as determined by Barnes and Maass (4).

In Fig. 1 the heat contents of one gram of "standard" cellulose are represented graphically. By plotting this curve on a large scale and taking tangents, the specific heats of cellulose were calculated, and are given in

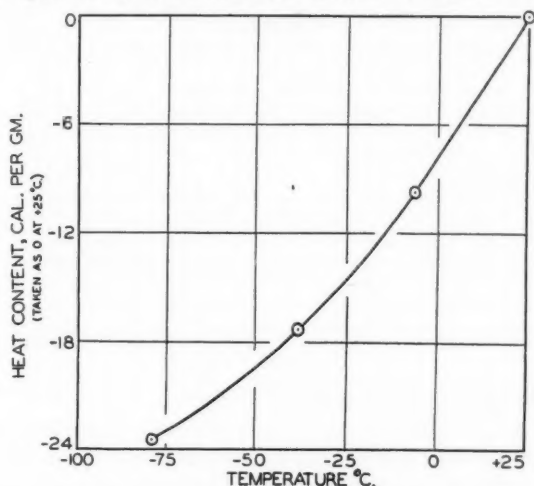


FIG. 1. Heat content of cellulose from $+25^{\circ}\text{C}$.

Table III. The only values for the specific heat of cellulose that have been published are those of Padoa (10), who gives a value of 0.347 between 0° and 80°C ., and of Fleury (7), who gives a value of 0.366 at room temperature. As a matter of interest the specific heats of dextrin and dextrose are also given in Table III. Dextrin has the same empirical composition as cellulose, while dextrose has one more molecule of water. The authors intend to redetermine the specific heats of these and other carbohydrate compounds for the same temperature range used for cellulose, as apparently some interesting conclusions might be drawn.

TABLE III
SPECIFIC HEATS

Temp., $^{\circ}\text{C}$.	Cellulose	Dextrin	Dextrose
-60	0.152		0.206
-40	0.187		0.230
-20	0.234		0.253
0	0.290	0.292	0.277
20	0.346	0.311	0.300

In Fig. 2 the heat content of free water is depicted in comparison with the heat contents of the "5.92%" water (Curve III) and "12.0%" water (Curve II). Curve I was obtained by subtracting Column 3 from Column 4, Table I, and recalculating on the basis of one gram of water. It, therefore,

represents what might be called the "12.0%" minus "5.92%" water. It is obvious that the latent heat of fusion is absent in the "5.92%" water, and the question arises whether this is due to supercooling or whether this water is not free water but in the nature of surface-combined water.

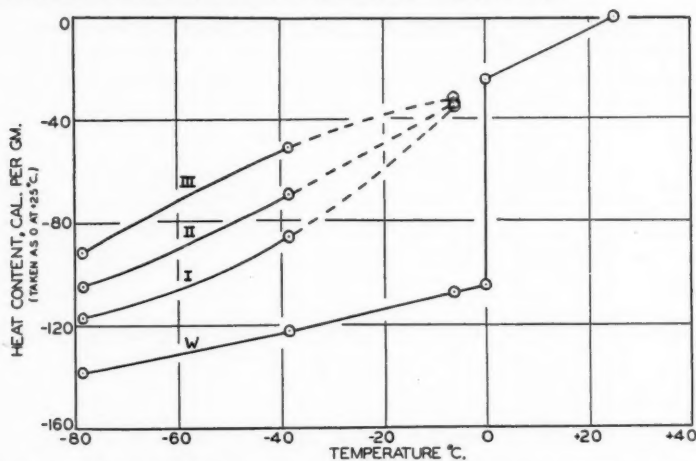


FIG. 2. Heat content of water from $+25^{\circ}\text{C}$. W, free water; I, "12% minus 5.92%" water; II, "12%" water; III, "5.92%" water.

Curve II appears to be continuous with the heat content curve of free water in the liquid state and would therefore point to the existence of supercooled water. Curve III indicates that this is fortuitous and that the problem is not quite so simple. The two taken together may indicate that some small part of the adsorbed water has a heat capacity that is lower than that of free water, and that the remainder exists in some other form partly in the solid state, the enhanced values in this region being due to a latent heat of fusion. Curve I indicates that something of the kind has taken place.

Further experiments will be necessary to determine what takes place in this region. For this purpose a more refined technique is being developed so that smaller amounts of adsorbed water can be examined with accuracy.

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STUDIES ON HOMOGENEOUS FIRST ORDER GAS REACTIONS

VI. THE DECOMPOSITION OF METHYLENE DIACETATE, METHYLENE DIPROPIONATE, AND METHYLENE DIBUTYRATE¹

BY C. C. COFFIN² AND W. B. BEAZLEY³

Abstract

The homogeneous decomposition of methylene diacetate vapor to formaldehyde and acetic anhydride at temperatures between 220° and 305° C. and at pressures ranging from several centimetres of mercury to several atmospheres has been studied. Reaction rates were determined by analytical and by pressure change methods. The first order decomposition is opposed by a second order recombination. A secondary reaction makes it impossible to determine the exact position of the resulting equilibrium. Within the rather large experimental error, methylene diacetate has the same activation energy (33,000 cal.) as its homologues. Its specific reaction velocity is smaller than that of the ethylidene esters. Methylene dipropionate and dibutyrate decompose at the same rate as the diacetate. These facts are in accord with the hypothesis that the extent to which a radical can contribute to the energy of activation is dependent upon its position in the molecule. Velocity constants are given by the equation $k = 1.7 \times 10^9 e^{-\frac{33000}{RT}}$.

Introduction

It has been shown in previous papers of this series (1, 2, 3) that esters represented by the formula $RCH(OOCR')_2$ decompose homogeneously in the gaseous state giving an aldehyde and an acid anhydride. The reaction, which takes place at a measurable velocity at temperatures between 200° and 300° C., is of the first order, and may be followed by rate of change of pressure at constant volume. It should be emphasized that the relatively low temperatures at which these decompositions attain a measurable rate eliminates the possibility of any free-radical chain mechanism, so that in all probability the primary reaction is a truly unimolecular process (6).

The general trend of the data already published (5) may be briefly summarized. Within experimental error the activation energy is a constant for the series. The addition of $-CH_2-$ groups to the aldehyde side (R) of the ester results in an increase in reaction rate, while such an addition to the hydrocarbon chains on the anhydride side (R') has little or no effect.

These data led to the use of the following hypothesis (2, 5) as a guide to further investigation. Energy can pass into a potentially reactive bond more readily from some parts of the molecule than from others. If the size and therefore the energy capacity of the part in good communication with this bond be increased, there will be an increased probability that this bond will acquire the energy necessary for its disruption. On the other hand, an increase

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of complexity in a part of the structure which is "insulated" from the reactive bond should not influence the chance of sufficient energy finding its way to the weak point of the molecule. From this obviously over-simplified point of view it would seem that the $-\text{CH}_2-$ groups on the anhydride side of the ester molecules do not easily exchange energy with the breaking bonds. The atoms on the aldehyde side, however, may act as energy reservoirs for the reaction.

As the constant activation energy and the wide variety of structural alterations possible in this series of compounds seemed to afford a good opportunity for studying the effect of molecular constitution on reaction velocity, a systematic search for empirical regularities was undertaken.

The present paper deals with the decomposition of methylene diacetate, dipropionate and dibutyrate to formaldehyde and the acid anhydrides. The activation energy is approximately the same as that previously found for other members of the series. The specific reaction velocity at any temperature is, as the above hypothesis would predict, smaller than that of esters made from higher aldehydes. Methylene dipropionate and methylene dibutyrate react at the same rate and with the same activation energy as methylene diacetate, so that here also the foregoing hypothesis receives experimental support.

An interesting feature of the methylene ester decompositions is that they do not go to completion at ordinary pressures, but proceed to a measurable equilibrium where the velocity of the second order recombination is equal to that of the first order decomposition.

Ester Preparation

Experimental

Methylene diacetate was prepared by absorbing formaldehyde vapor in hot acetic anhydride containing a trace of sulphuric acid. After the catalyst had been neutralized with sodium acetate, the ester was purified by a method similar to that used in the case of butylidene diacetate (3). Three different preparations, all boiling at temperatures between 167° and 168°C. , were made from formaldehyde and anhydride from different sources. All three decomposed at the same rate. The dipropionate and the dibutyrate were made by absorbing formaldehyde vapor in the respective anhydrides.

Apparatus and Technique

Reaction velocities were determined by two different methods.

(1) A weighed quantity of ester in a glass capsule was sealed inside an evacuated reaction tube the volume of which was determined after the experiment. After a known time at a definite temperature (the vapor of benzophenone boiling under a constant pressure) the tubes were removed, broken under distilled water, and analyzed for acetic anhydride.

(2) At pressures below atmospheric the rate of change of pressure at constant volume was determined in an apparatus already described (4).

For runs at pressures between 1 and 3 atm. the apparatus shown in Fig. 1 proved to be very satisfactory. Two similar tubes *A* and *B* (capacity 80–100 cc.) were joined together at the bottom by a short capillary U-tube. A three foot length of heavy barometer tubing, *C*, was sealed to the other end of *A*.

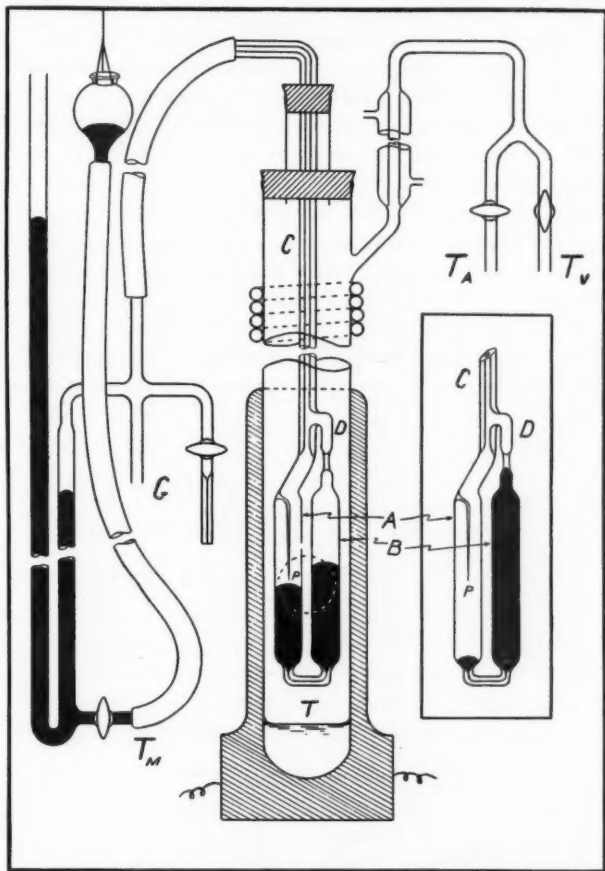


FIG. 1. Diagram of high pressure apparatus.

Both tubes were filled to slightly more than half their volume with distilled mercury, and a capsule containing a weighed amount of ester was dropped into the open end of *B*, which was then sealed to a side arm *D* on the tube *C*. When the apparatus had been evacuated (through *C*), *D* was heated and allowed to collapse so that *B* was separated from *C*. The closed tube *D* is left joining *B* and *C* for greater mechanical strength. *A* may now be opened to the atmosphere and the mercury forced into *B*.

To make a run, *C* is connected with rubber pressure tubing to a carbon dioxide cylinder (at *G*) and a long manometer, and the whole apparatus is

lowered into the thermostat T —a large Pyrex "test tube" containing benzo-phenone boiling at atmospheric pressure. A rubber stopper near the top of C fits tightly into the end of this tube, which can be connected through a side arm and condenser to a pump, manometer, and a 20-litre stabilizing volume. As soon as the thermostat is stoppered it is connected to this volume, and the pressure is set to that corresponding to the temperature desired. When the bulb breaks and the ester vaporizes, the pressure in A is adjusted by means of the carbon dioxide cylinder until the mercury surface is at the pointer P , where it is kept throughout the reaction, which is followed by the rate of pressure increase.

Results

In Fig. 2 the percentage reaction in one hour at 290°C . as determined by analysis is plotted against calculated initial pressure. The decrease in decomposition with increase of pressure suggests that the reaction does not go to completion. That this is actually the case is evident from Fig. 3. in which percentage reaction at 279°C . is plotted against time. The lower curve represents the ester decomposition, and the upper curve, the percentage

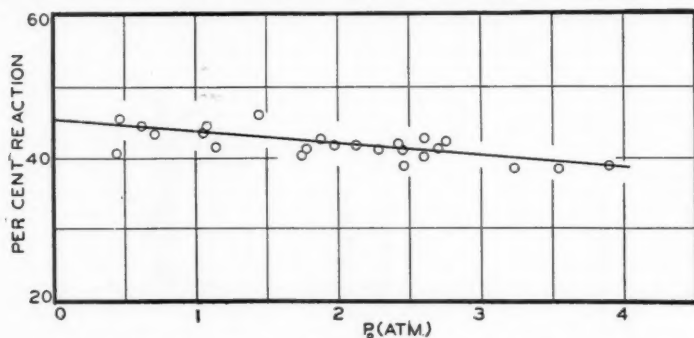


FIG. 2. Percentage reaction in one hour at 290°C .

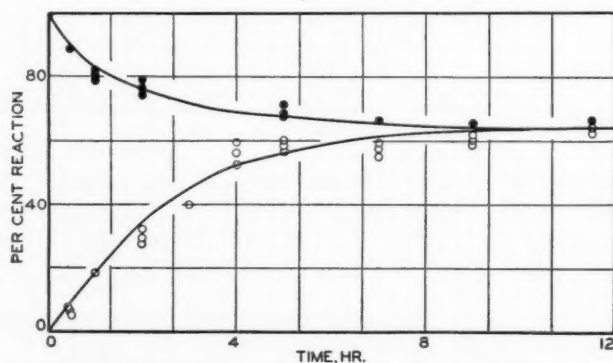


FIG. 3. The system formaldehyde-acetic anhydride-methylene diacetate. Temp., 279°C . Equilibrium pressure, about 5 atm. ●, Association. ○, Dissociation.

reaction in an equimolecular mixture of formaldehyde and acetic anhydride. Reactant quantities and bulb volumes were such that the final equilibrium pressure in each case would have been between 5 and 6 atm. The existence of a true equilibrium corresponding under these conditions to about 35 mole per cent ester is unmistakable.

The determination of the decomposition velocity constants by rate of pressure change is somewhat complicated by the presence of this reverse reaction. A more troublesome correction arises from the fact that a consecutive reaction (probably a heterogeneous decomposition of formaldehyde) prevents the system from reaching a steady final pressure. The following method was finally adopted for estimating velocity constants from observed pressure changes.

The reaction being of the type $AB \rightleftharpoons A + B$, the velocity equation will be

$$-\frac{d[AB]}{dt} = k_1[AB] - k_2[A][B].$$

If the partial pressures of ester aldehyde and anhydride expressed in terms of total pressure, P , and initial pressure, P_0 , are substituted for concentrations, the expression becomes

$$\frac{dP}{dt} = k_1(2P_0 - P) - k_2(P - P_0).$$

Substituting Kk_1 for k_2 and integrating, we have

$$k_1 = \frac{2.3K}{Ct} \log \frac{(P - 3P_0)K - (P - P_0)C}{(P - 3P_0)K + (P - P_0)C},$$

where K is the equilibrium constant and $C = \sqrt{K^2 + 4P_0K}$.

The fact that the system does not reach a steady final pressure makes it impossible to determine K directly. An indirect estimation of sufficient accuracy for the present purpose may be obtained from a consideration of the rate, k' , at which the system moves toward equilibrium. This rate is given by the equation

$$k' = k_1 + k_2 = \frac{2.3}{t} \log \frac{P_F - P_0}{P_F - P},$$

where P_F is the final equilibrium pressure. The true value of P_F may be taken as that value (determined by trial and error) which will make the graph of $\log \frac{P_F - P_0}{P_F - P}$ against time a straight line over the first 50 to 60% of the reaction. This calculated P_F is used to evaluate K , and hence k_1 and k_2 . The large uncertainty in the equilibrium constant obtained in this way is not so serious in the velocity constant where K appears as a correction term.

Many unsuccessful attempts were made to find a catalyst for the reaction in order to determine K directly and more accurately over a wider temperature range. The presence of mercury, glass surface, oxygen, water vapor, hydrogen chloride, sulphur dioxide, or iodine was found to have no measurable effect on the reaction rate as determined by analysis. A greenish brown

fluorescent film formed slowly on the walls of the reaction tubes whether or not a "catalyst" was present, and in most of the bulbs a few cubic centimetres of a water insoluble gas was formed. Several microanalyses showed this gas to be mostly carbon monoxide and hydrogen, so that the consecutive reaction interfering with the velocity and equilibrium measurements is probably a heterogeneous decomposition of formaldehyde or of one of its polymers.

While any one experiment gave fairly consistent rate constants, the results of different runs are so scattered that it is sufficiently precise to report the data graphically. Fig. 4 shows the total pressure plotted against time for

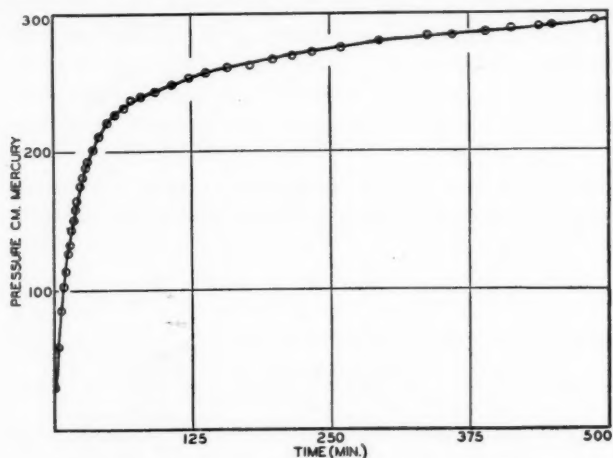


FIG. 4. Data of typical methylene diacetate run.

a typical run (made with the apparatus of Fig. 1; methylene diacetate, $P_0 = 115$ cm. of mercury; $T = 579^\circ \text{C.}$) The time axis is compressed to indicate the difficulty of determining the true final pressure. In Fig. 5, which includes the results of all the 60 runs on the three esters made by pressure

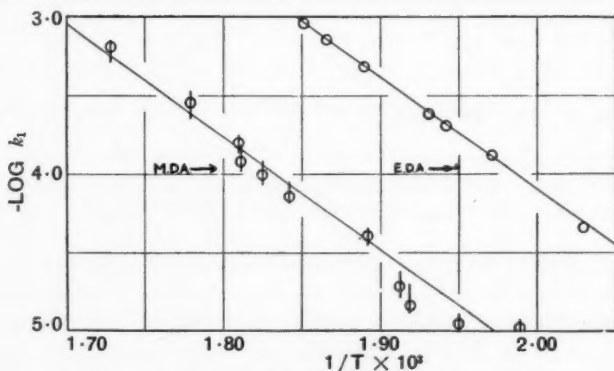


FIG. 5. $-\log k_1$ plotted against $1/T$.

change methods, $-\log k$ is plotted against $1/T$. The lower line refers to the methylene esters, while the upper represents the previously determined (2) data for ethylidene diacetate. The methylene points give the mean of the results at the respective temperatures. The vertical lines through the points indicate the range covered by these results. Initial pressures varied from 0.1 to about 3 atm.

The straight line through the methylene points has arbitrarily been given the same slope as that through the ethylidene points. It is evident that within the unfortunately large experimental error of from 10 to 20%, the activation energies are the same. On account of the fact that the uncertainties due to incomplete decomposition and the consecutive reaction probably vary widely with both pressure and temperature, it is impossible, without the statistical treatment of an inconveniently large number of experimental results, to estimate the errors with any degree of accuracy. All that can be said with certainty at present is that methylene diacetate, dipropionate, and dibutyrate decompose at rates and with activation energies that are practically identical. This reaction rate is about $\frac{1}{12}$ that of ethylidene diacetate at any temperature. The straight lines of Fig. 5 are given by the following equations.

$$\text{Ethylidene diacetate: } k = 2 \times 10^{10} e^{-\frac{33000}{RT}}$$

$$\text{Methylene diacetate, etc.: } k = 1.7 \times 10^9 e^{-\frac{33000}{RT}}$$

In connection with the reverse reaction, it is of interest to attempt an estimate of the proportion of "activated" collisions that result in the formation of ester molecules. This amounts to determining the factor P in the equation $k_2 = PZe^{-E/RT}$, where Z is the number of collisions. At 562° C. the equilibrium constant in atmospheres, Kp , has a value of about 2 for methylene diacetate. (Kp is appreciably smaller in the case of the dipropionate and the dibutyrate.) If atmospheres are converted to moles per litre, the constant, K , becomes 0.04, which makes k_2 equal to 7×10^{-3} litres mole⁻¹ sec⁻¹. ($k_1 = 3 \times 10^{-4}$ sec⁻¹.) The heat of reaction is unknown (the values of Kp are too uncertain to permit calculation of ΔH), but is probably about 6000 cal. per mole, so that $E_2 = 33,000 - 6000 = 27,000$ cal. approximately. If a mean molecular diameter of 5×10^{-8} cm. is assumed, it is found that k_2 should be about 11 if every collision between activated molecules results in reaction. It thus appears that P is roughly 10^{-3} , or that only about 1 in every 1000 collisions between activated formaldehyde and acetic anhydride molecules leads to ester formation. This preponderance of unfruitful collisions is probably due to the necessity of fulfilling some rather exacting conditions of orientation or phase synchronism at the moment of impact. It is perhaps significant that the A -factor of the first order decomposition is also smaller by about 10^3 than that usually found experimentally for unimolecular reactions, or calculated from Rice and Gershinowitz' hypothesis of "exact orientation" (7). A detailed investigation of the association reaction is in progress.

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